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OIL POLLUTION
CONTROL TECHNOLOGY

This course is offered for employees of regulatory agencies who are assigned direct responsibility for response to nonrecurring discharges of oil. It is not intended to dictate arbitrary solutions to technical problems in spill control but will familiarize students with alternatives and provide opportunity to practice response under realistic constraints and measures of success. In particular, students who complete this course will be able to function within the guidelines of federal, state, or interstate Contingency Plans in effect in the area where the course is presented.

ENVIRONMENTAL PROTECTION AGENCY
EDISON WATER QUALITY LABORATORY
TRAINING PROGRAM

FEBRUARY 1971

FOREWORD

These manuals are prepared for reference use of students enrolled in the Oil Pollution Control Technology Training Course presented at the Edison Water Quality Laboratory.

Due to the limited production and availability of the manuals, it is not appropriate to cite them as technical references in bibliographies or other forms of publication.

References to products and manufacturers is for illustration only; such references do not imply product endorsement by the Environmental Protection Agency.

The reference outlines in this manual have been selected and developed with a goal of providing the student with a fund of the best available current information pertinent to the subject matter of the course. Individual instructors may provide additional material to cover special aspects of their own presentations.

This manual will be useful to anyone who has need for information on the subjects covered. However, it should be understood that the manual will have its greatest value as an adjunct to classroom presentations. The inherent advantages of classroom presentation is in the give-and-take discussions and exchange of information between and among students and the instructional staff.

Constructive suggestions for improvement in the coverage, content, and format of the manual are solicited and will be given full consideration.

G. F. McKenna
Regional Training Officer
Edison Water Quality Laboratory
Environmental Protection Agency

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OIL SP'LL PROBLEM

Magnitude of Oil Problem

Refinery and Terminal Operations

Platform Operations

Biological Effects

OIL POLLUTION: MAGNITUDE OF THE PROBLEM

I SOURCES AND AMOUNTS

A Broad Picture

Petroleum in its many forms has been on the move in the United States since 1859 when the first commercially successful oil well was developed in Pennsylvania. First transported by wagon and log raft, oil is now en route from the oil field to refinery to consumer by pipe, water, rail and highway. During 1970 more than 4.5 billion barrels of petroleum moved as crude oil from the production field through the refineries and then as refined products to the consumer. Ocean tankers, barges, pipelines, railroad tank cars and tank and trucks are the vital elements of the complex and diversified transportation system required to move this volume of oil.

Estimated amounts of oil lost⁽¹⁾ as well as the sources of this form of pollution are shown in Table I. It is interesting to note that the loss of waste or used oil from vehicles (crankcase oil) may be the largest single source of oil pollution, larger, in fact, than the total volume from all sources lost directly to the oceans.

B Spill Frequency

Obtaining of one barrel of petroleum from the oil field to the consumer may require 10 to 15 transfers between as many as six different transport modes. Each mode is subject to accidents, and

at the transfer points spill frequency is extremely high. Approximately one barrel of product is lost for each one million transported. About 7,500 oil spills⁽²⁾ are now occurring annually with an estimated total loss of 500,000 barrels⁽³⁾. Most of the spilled oil is discharged to water. In addition to spills, the potential for discharges from normal vessel operation is in excess of 700,000 barrels⁽⁴⁾ of oil annually.

The number of spills and quantities lost vary with the type of transport system. About 217,000 miles of petroleum pipelines crisscross the United States transporting 45 percent of the Nation's annual consumption of petroleum. Pipeline failures accounted for only three percent⁽³⁾ of the product lost in 1969.

A United States fleet of 387 tankers and 2,900 barges presently operates in the Nation's waterways. In worldwide oil traffic, United States vessels make up only five percent of tanker traffic⁽⁴⁾. United States and foreign flag tankers were responsible for approximately 80-90 percent⁽³⁾ of the oil spilled in 1969.

Tank trucks and railroad tank cars together account for less than one percent⁽³⁾ of total product lost.

Tank trucks are the last leg of the transportation system, delivering refined products to the retail consumer. Approximately 158,000 tank trucks are on the road. In areas not served by pipelines or navigable waterways, over 81,000 railroad tank cars take over the transport of crude and refined petroleum products.

TABLE I
ESTIMATES OF OIL INTRODUCED
INTO WORLD'S WATERS AND POTENTIAL LOSSES TO
WATERS, 1969

Metric Tons Per Year		% of <u>Total</u>
1. Tankers (normal operations)		
Using Control measures (80%)	30,000	
Not using control measures (20%)	<u>500,000</u>	
	530,000	10.7
2. Other ships (bilges, etc.)	500,000	10.1
3. Offshore production (normal operations)	100,000	2.0
4. Accidental spills		
Ships	100,000	2.0
Nonships	100,000	2.0
5. Refineries and petrochemical	300,000	6.0
SUBTOTAL	1,630,000	
6. Potential losses to water from industrial and auto- motive (not fuel):		
Highway vehicle spent oils	1,800,000	36.6
Industrial plus all other vehicles	<u>1,500,000</u>	30.6
SUBTOTAL	<u>3,300,000</u>	
TOTAL	4,930,000	

NOTE: Oil from pleasure craft and natural seeps not included.

C Why Spills Occur

Blumer (1969) reported that human error accounted for 88 percent of the total number of spill incidents. The means of rectifying this situation is by better training and education, improved engineering, and when all else fails enforcement by a responsible state or federal agency.

Another important factor in the cause of spills by vessels is the stopping ability of the tankers under crash stop conditions — vessel in full reverse. It has been reported that ⁽⁵⁾ the most important factor in connection with collision and stranding — the two most dreaded casualties — is the 'crash stop' ability. Unfortunately, the ability of tankers to come to a 'crash stop' has decreased as their size has increased. For the 400,000 tonner, the straight-line stopping distance for a 'crash stop' would be four to five miles and would take approximately 30 minutes. During this period of backing full, the ship's master is unable to steer her or regulate the speed. If the engines are not put 'full astern' but on 'stop' it takes up to one hour for the 'Universe Ireland' to come to a stop.

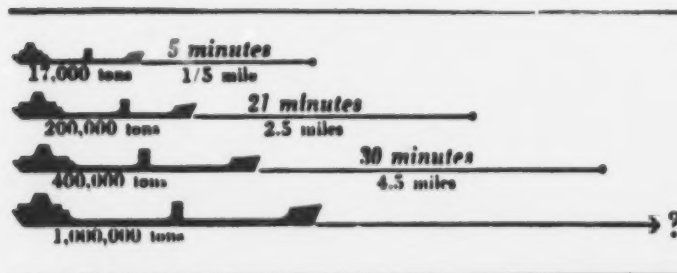


Figure 1

II ANALYSIS OF PAST MAJOR SPILLS

Dillingham Corporation (1969), under contract to API, conducted a statistical study to develop an understanding of the basic characteristics of major oil spills — defined as a spill of 2,000 barrels (84,000 gallons) or more of a heavy (or persistent) oil which will not naturally evaporate or disperse rapidly in the environment — and thus define the nature and scope of the problem.

Based on an analysis of 38 past spills, which occurred during the period 1956 to 1969, they reported that:

A Source

75% were associated with vessels, principally tankers.

B Composition

90% involved crude or residual oils.

C Volume

70% of the spills were greater than 5,000 barrels with a median spill volume of 25,000 barrels.

D Distance Offshore

80% occurred within 10 miles of shore and the oil would reach shore within one day.

E Duration

75% of the spill incidents lasted more than five days with a median duration of 17 days.

F Extent

80% contaminated less than 20 miles of coastline with a median extent of four miles of coast.

G Coastline

85% occurred off shoreline considered to be recreational.

H Distance from Port

75% occurred with 25 miles of the nearest port.

Item (D) above is probably one of the most significant factors revealed by this study. As shown in Figure II, fifty percent of the offshore spills occurred less than one mile from shore. Since oil appears to drift at approximately 3% of the wind velocity, and with an assumed average wind of 15 knots, the oil slick would drift at approximately 0.5 knots. Thus, with 50% of the spills less than one mile offshore, an onshore wind could move oil onto shore in two hours. The question that now arises is "how does one mobilize shoreline protection equipment during this short length of time?"

III MAJOR SPILL INCIDENTS 1956-1970

For reference purposes, major spill incidents along with significant characteristics, are shown in Table II.⁽⁴⁾

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Distance from Shore and Response Time *Available for Shoreline Protection* *Data from 25 Incidents*

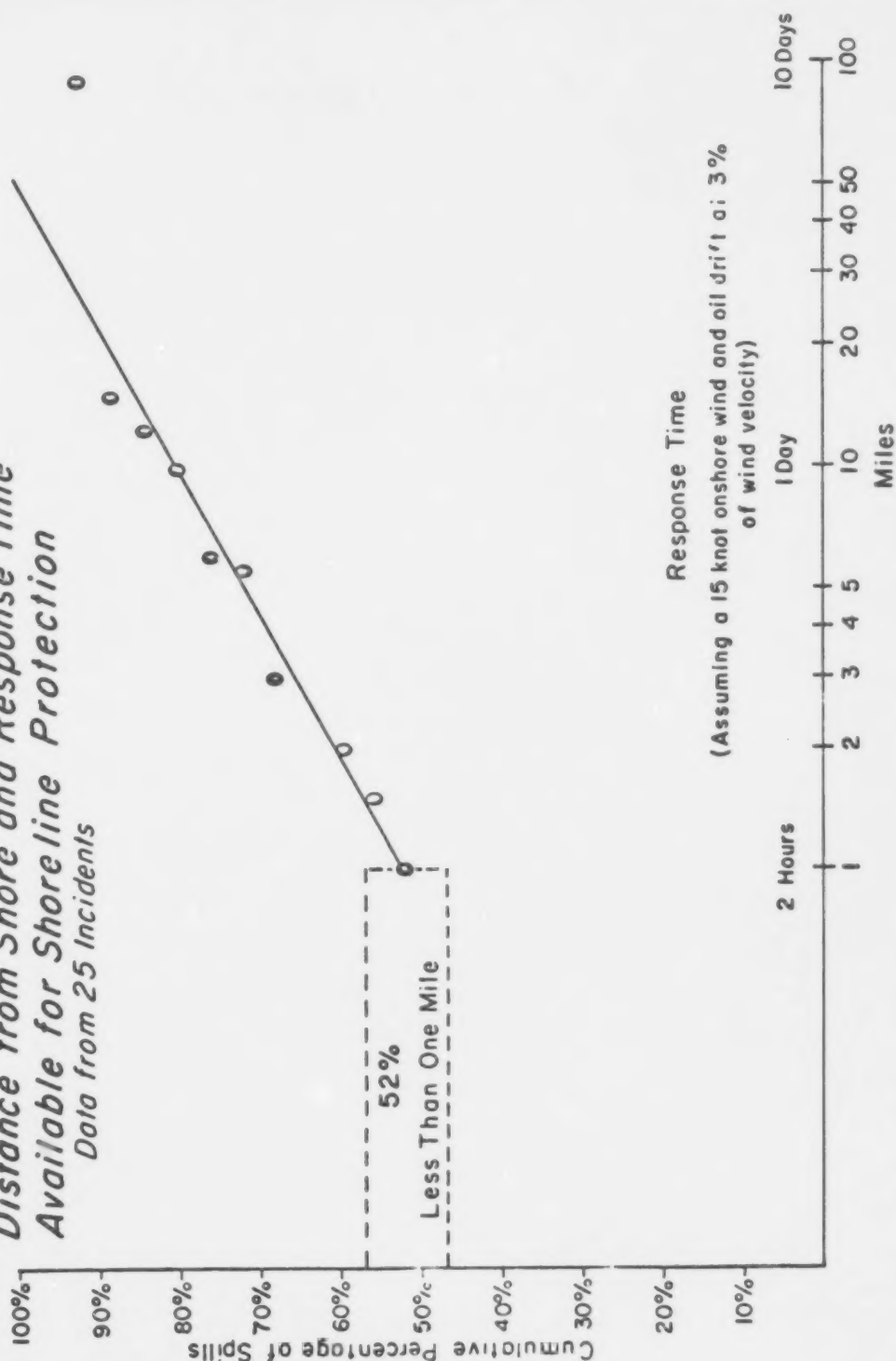


TABLE II
MAJOR OIL SPILL INCIDENTS

<u>Name</u>	<u>Date</u>	<u>Cause of spill</u>	<u>Material</u>	<u>Volume (barrels)</u>
ALGOL, tanker	02-09-69	Grounding	#6 F. O.	4,000
ANDRON, tanker	05-05-68	Sinking	Crude	117,000
ANNE MILDRED BROVIG, tanker	02-20-66	Collision	Crude	125,000
ARGEA PRIMA, tanker	07-17-62	Grounding	Crude	28,000
ARROW, tanker	02-04-70	Grounding	Residual	36,000
BENEDICTE, tanker	05-31-69	Collision	Crude	14,000
Bridgeport, Conn., terminal	6-15-70	Pumping	#2 F. O.	20,000
Chester Creek, pipeline	08-08-69	Break	#2 F. O.	3,500
CHRYSSI P. GOULANDRIS, tanker	01-13-67	Unknown	Crude	2,600
Dutch Coast Spill	02-16-69	Unknown	Residual	1,000
ESSO ESSEN, tanker	04-29-68	Grounding	Crude	30,000
ESSO HAMBURG, tanker	01-29-70			10,000
FLORIDA, barge	09-16-69	Grounding	#2 F. O.	4,000
GENERAL COLOCOTRONIS, tanker	03-07-68	Grounding	Crude	30,000
HAMILTON TRADER, tanker	04-30-69	Collision	Residual	5,000
HESS HUSTLER, tank barge	11-12-68	Grounding	#6 F. O.	40
Humboldt Bay, refinery	12- -68	Hose failure	Diesel	1,400
KENAI PENINSULA, tanker	11-05-68	Collision	Crude	1,000
KEO, tanker	11-05-69	Hull failure	#4 F. O.	210,000
Louisiana, Chevron platform	04-10-70	Fire	Crude	60,000
Louisiana, Shell platform	12-1-70	Fire	Crude	Unknown as of this date
MARTITA, tanker	09-20-62	Collision	Bunker C	4,300
Moron, refinery	03-29-68	Pumping	Crude	16,000
New Castle, power station	1963-65	Leak	Residual	40
OCEAN EAGLE, tanker	03-03-68	Grounding	Crude	83,400
R. C. STONER, tanker	09-06-67	Grounding	Mixed	143,300
Refinery Loading Site	1962	Hose failure	Crude	2,000
ROBERT L. POLLING, tank barge	05-10-69	Collision	#2 F. O.	4,700
Santa Barbara, platform	01-28-69	Natural faults	Crude	100,000
Schuylkill River, Berks Assoc.	11-13-70	Lagoon failure	Waste Crankcase	70,000
Sewaren, N. J., storage tank	10-31-69	Tank failure	Crude	200,000
Ship Shoal, drill rig	03-16-69	Storm shifting	Crude	2,400
Staten Island, N.Y., 2 Esso barges	05-22-70	Collision	#6 F. O.	10,000
USS SHANGRI-LA (CVA-38)	1965	Pumping	NSFO	200
TAMPICO, tanker	03- -57	Grounding	Diesel	60,000
TIM, tank barge	02-18-68	Sinking	#6 F. O.	7,000
TORREY CANYON, tanker	03-18-67	Grounding	Crude	700,000
Waikiki Beach	04-21-68	Unknown	Bunker C	
Waterford Beach	01-18-69	Unknown	#6 F. O.	
WITWATER, tanker	12-13-68	Hull failure	Mixed	15,000
WORLD GLORY, tanker	06-13-68	Hull failure	Crude	322,000

REFINERY AND TERMINAL OPERATION

I INTRODUCTION

- A A petroleum refinery is an organized and coordinated arrangement of manufacturing processes designed to provide both physical and chemical change of crude petroleum into saleable products with the qualities required.

II TYPES OF REFINERIES

- A Refineries can be classified as simple, complex, or fully integrated.
 - 1 A simple refinery will include crude oil distillation, catalytic reforming and treating. Its products will be limited to LP gas, motor fuels, kerosene, gas oil, diesel fuel and fuel oil.
 - 2 A more complex refinery will make a greater variety of products and require the following additional processes: vacuum distillation, catalytic cracking, polymerization, alkylation and asphalt oxidation.
 - 3 The fully integrated refinery makes a full range of products. Additional products will include lubricating oils, greases, and waxes. Additional equipment will include solvent extraction, dewaxing and treating.
- A typical refinery flow plan for a fully integrated refinery is presented as Figure 1.

III TYPES OF CRUDE OILS

There are over 8,000 different types of crude oils in the USA alone and these vary from high to low sulfur content and from asphaltic to paraffinic and from heavy to light in specific gravity.

- A The asphalt base crudes contain very little paraffin wax and a residue primarily asphaltic. These crudes are particularly suitable for making high quality gasoline and asphalt.
- B Paraffin base crudes contain little asphaltic material, are good sources of paraffin wax, quality motor oils, and high grade kerosene.
- C Mixed base crudes contain both wax and asphalt. Virtually all products can be obtained.

IV TYPES OF PROCESSES

A Atmospheric Distillation

Today's crude distillation occurs in towers containing a series of horizontal trays where liquid condenses, collects and is withdrawn. Since distillation is the most frequently used unit operation in refining, a drawing of a typical

distillation column is presented as Figure 2.

The lighter, more volatile portions of the crude are withdrawn at the upper part of the tower and the heavier parts down lower in the tower. Improved separation between products can be accomplished by installing more fractionating trays. It is in this manner that the crude oil is first broken into its parts.

B Vacuum Distillation

Normally, it is desired to cut deeper into the crude oil than would be possible under atmospheric pressure and reasonable temperatures. Therefore, vacuum distillation is performed on the residual from the atmospheric distillation. This process is essentially the same as atmospheric distillation except it is fractionation performed under a vacuum.

C Catalytic Cracking

The rising needs for producing more gasoline per volume of crude oil led to the development of catalytic cracking. Here, a gas oil, not valuable for any other use, is fed to the catalytic cracking unit where it is cracked in the presence of a catalyst to gasolines and heating oils.

D Alkylation

Further needs for high octane gasolines led to the development of another process called

alkylation where several components of the refinery gas streams are combined over a catalyst to make a high octane component.

E Polymerization

Here, again, this process was developed to utilize several components from a normal refinery gas stream and combine them into high octane number gasoline fractions.

F Platforming

This major process development consisted of the use of a platinum based catalyst to upgrade the octane number of naphtha distilled from crude oil to very high levels for use in aviation and high quality motor fuels.

G Hydrotreating

This process utilizes the excess hydrogen produced in the platforming process to remove sulfur compounds in many refinery products, motor fuel, lube oil and fuel oil.

H Hydrocracking

The use of hydrogen was extended to the hydrocracking process which converts petroleum residues by catalytic hydrogenation to refined heavy fuel oils or to high quality catalytic charge stocks.

I Coking

In this process heavy low grade oils are converted into lighter products and coke which is sold or burned.

J Treating Process

Many contaminants are present in crude oils in varying concentrations and include organic compounds containing sulfur, nitrogen and oxygen, dissolved metals and inorganic salts. These contaminants are removed at some intermediate stage or just prior to sending the finished product to storage. Numerous treating chemicals are used and most fall into one or more of these classifications:

- 1 Acid
- 2 Alkali
- 3 Solvent
- 4 Oxidizing agent
- 5 Absorption agent

V EFFLUENT WATER IMPROVEMENT PROCESSES

A API Separator

This equipment removes surfaced oil by skimming and pumping the skimmed oil to rerunning.

B Equalization Basin

Secondary oil recovery is possible here because of the large holding time.

C Flocculator-Clarifier

Coagulants are used to break emulsions and oil is removed by skimming.

D Biological Treatment

The activated sludge uses dispersed air for mixing and oxygen supply. The water can also be treated in trickling filters which are packed with high rate plastic media.

E Holding Basins

These basins are utilized to permit checking the quality of the effluent. If not satisfactory, it can be recycled.

F Ozonator

Here the phenols are reduced by oxidation and the water is partially sterilized.

G Activated Carbon and Rapid Sand Filtration

Here additional reduction of phenols is accomplished by mixing the activated carbon with the waste streams and removing it in sand filters.

VI TERMINALLING

A Tankers

- 1 Tankers are loaded or unloaded through flexible hose connected to shore

pipelines or by means of loading booms made of conventional pipe connected by swivel joints.

2 Tankers are divided into two groups:

- a Dirty or black oil ships which transport crude oils, fuel oils and diesel fuels.
- b Clean or white oil ships which carry highly refined products.

B Barge

- 1 Another form of transport is the barge usually used on long wide navigable rivers. Barges usually carry products rather than crude oil.

C Procedure for Handling Receipts

- 1 A discussion between the vessel people and terminal people should be held as soon as the vessel is properly hooked up. Sequence of discharging lines to be used, volume of each product and permissible pressure must be clearly understood.

2 Communications

Appropriate signals and means for transmitting them must be established. Telephone or

walkie-talkies or hand radios can be utilized.

The vessel dock officer must be notified whenever a change in receiving tankage is to be made so he can prepare for a pressure surge.

3 Identification of Lines

All lines and manifolds should be clearly marked so that the pipelines carrying each product are identified.

4 Manning

It is prudent operation to maintain one man on the terminal side of the facilities at all times and one man on the ship at all times so that in the event of an emergency the proper steps can be taken by each immediately.

5 Vessel Check

Prior to starting the ship's pumps or notifying the dock crew to begin transfer operations, the senior deck officer must assure himself that the entire cargo system is lined up properly.

6 Terminal Check

The terminal superintendent or his representative should be certain that all valves controlling flow to and from tanks involved in the discharge or loading are in their proper setting and that valves not involved in the transfer or loading are closed.

7 Use of Log

The use of a log reading the amount that the tank has received and comparing this volume with the amount that the tanker has discharged every two hours will quickly inform the terminal personnel that all material is finding its way into proper tankage or not.

8 Topping Off and/or Switching Tanks

Terminal manpower should always be assigned when the level of oil in a tank reaches a high point in that tank.

9 Tankage Assignment

Before the cargo arrives, it is important that the terminal people in charge of the receipt check the volume of space available to receive each product and conclude whether adequate space is available. This information should be entered on the log as the stop-gauge for the transfer for each specific products.

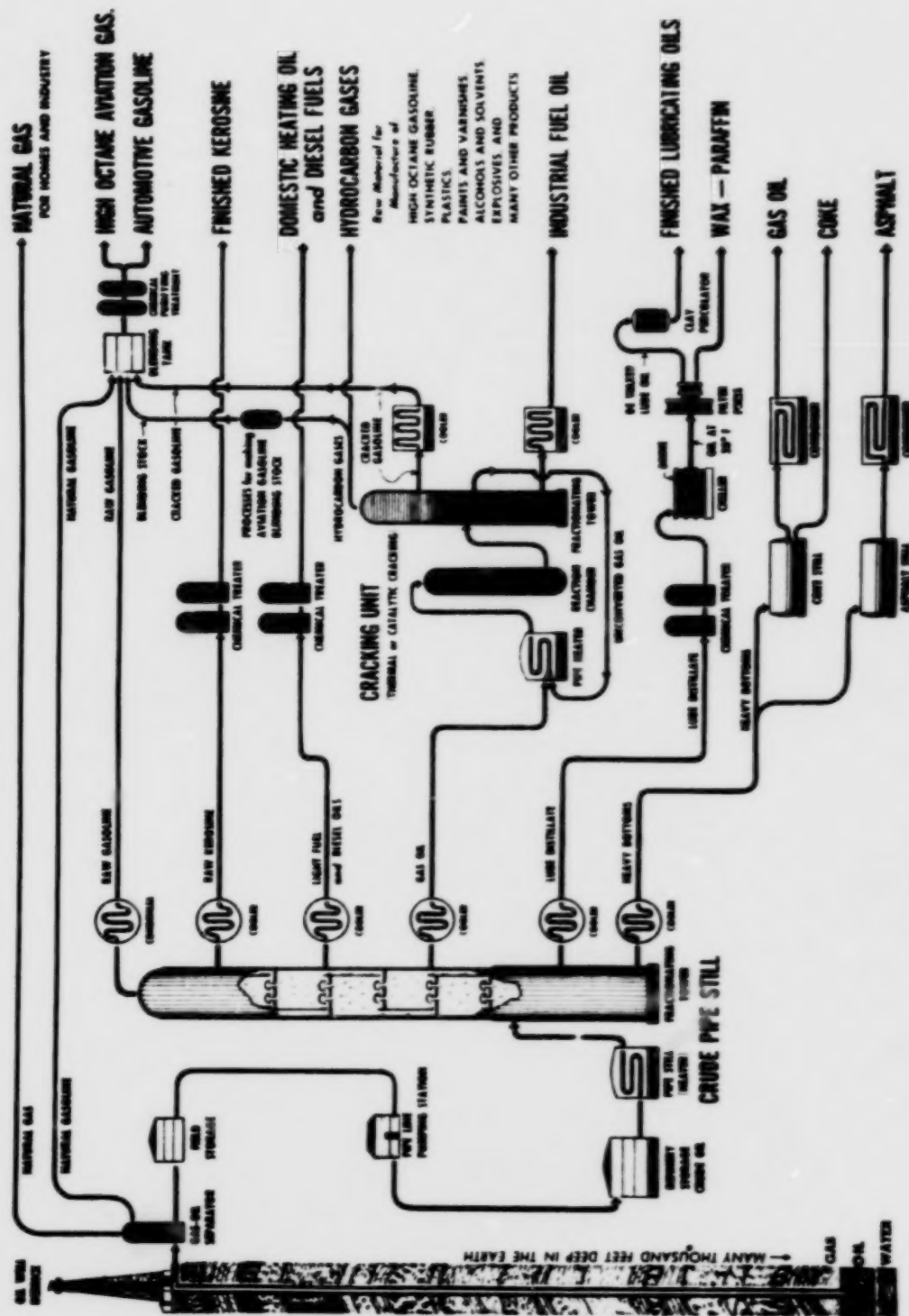


Fig. 1 Simplified flow Diagram of Refinery

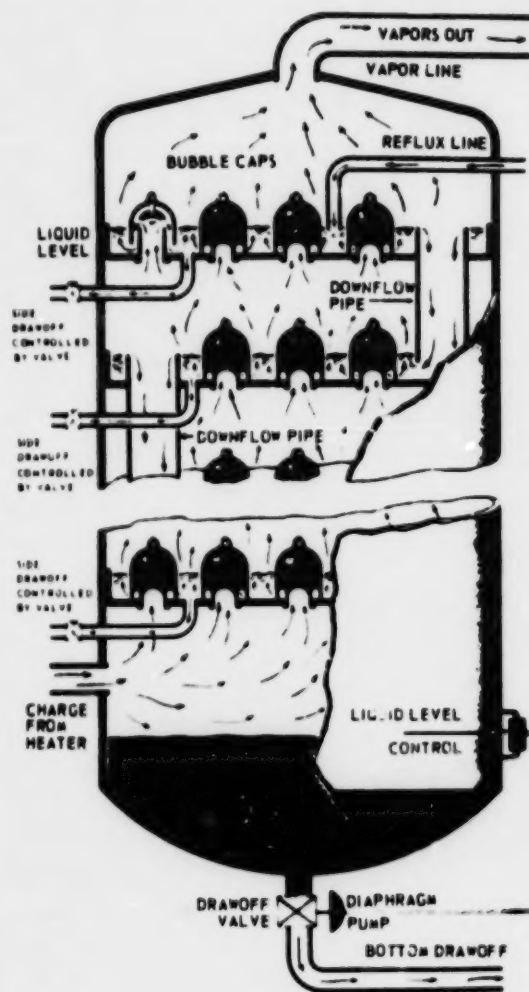


Fig. 2 - Bubble Cap-type Fractionating Tower

PLATFORM OPERATIONS

I INTRODUCTION

- A More than 100 companies are now active in offshore petroleum, operating off the coasts of 75 countries. The value of the work in progress is about \$3 billion and at the end of 1970, the total investment in the offshore oil industry has amounted to about \$20 billion.

Daily offshore U. S. production is in the range of 1.30 million barrels of oil, representing 14.5% of the domestic total. Proved reserves of offshore oil stand at 85 billion barrels, or about 20% of the estimated world inventory of 425 billion barrels.

In 1969 approximately 1,160 wells were drilled in the offshore U. S. areas. At the present time there are 2,564 offshore platforms, structures and facilities in The Gulf of Mexico, off the California coast and in the waters of Alaska. Of this number, 764 are in navigable (3 miles from shore) waters. Even though water is not discharged from all these platforms, structures and facilities, they do constitute a potential source of pollution due to blow-outs and other accidents.

- B Current practice in the offshore oil industry is to group platforms, structures and facilities, located in particular fields, for economy in operation. Thus, for example, one main platform may serve as the supporting facility for ten or more structures. This

main platform then provides living quarters, office space, treatment facilities and control centers for the other structures in the group. At an average bare-bones cost of \$8 million, real estate on these main platforms runs about \$40 per square foot with an average surface area of 200,000 square feet. These surface areas and cost figures play an important role in the selection of water treatment equipment.

II TREATMENT OFFSHORE

- A The original carboniferous deposits accumulating within, or at the edge of, ancient seas constituted the beginning of petroleum formations. It therefore follows that some part of those ancient seas will be produced with the oil and gas today. This water, which accumulates during the production processing of oil and gas, is frequently great in volume sometimes exceeding 20,000 barrels per day for one field. This water may constitute from less than 10% to greater than 50% of the total fluids produced from a single well.

Depending on several variables, an offshore operator may decide to:

- 1 Pump the entire oil/water mixture to shore for treatment.

2 Pump the oil/water mixture to shore for treatment following a free-water knockout process.

3 Treat the oil/water mixture on the platform and sell the oil to a pipeline company at the platform.

This last choice requires that the oil contain a maximum of 2% water and generally no more than 1% water.

The variables upon which the above decisions are based include:

- 1 Distance to shore - 20 to 30 miles is generally the maximum.
- 2 The presence and types of solids and emulsions concerned.
- 3 The relative specific gravity of the oil and water.
- 4 The chemical characteristics of the oil - the paraffin content plays an important role.
- 5 Economics of treating on shore vs. on the platform.
- 6 The percent of water produced with the oil.

Treatment equipment must take into account the fact that the above variables change with time. This requires that adequate safety factors be included in design calculations.

B There are two basic types of equipment associated with oil/water separation on off-shore production facilities:

- 1 Operation equipment.
- 2 Conditioning equipment.

Operation Equipment — That equipment used in the process of separating well gas from fluids and processing fluids to remove WATER from the OIL. Depending upon the throughput volume in operation equipment, and also upon the presence and types of solids and emulsions concerned, the character of the various emulsifying agents and the relative specific gravity of oil and water, the oil contamination in the separated water will frequently be from 200 ppm to 3,000 ppm or more. As the water content in the product oil decreases, the oil content in the effluent water increases. Therefore, the 2% maximum (and 1% desired) water content required by the pipeline company has a direct bearing on the amount of oil that must be removed from the discharge, or bleed, water.

Process units that may be classified as Operation Equipment include the following:

- 1 Emulsion treaters.

2 Heater treaters.

3 Free-water knockouts.

4 Phase separators (gas, water and oil).

Prices for this equipment range from \$3,000 for a 12,600 gallon free-water knockout separator (4 hour detention time) to \$52,000 for a heater treater handling 10,000 barrels per day.

The free-water knockout and phase separators are essentially sedimentation tanks wherein the gas, oil and water separate by gravity under pressure. Valves, located at the phase interfaces, draw off the particular components. The emulsion and heater treaters make use of emulsion breakers (either chemical or heat) to more effectively remove the water phase.

Conditioning Equipment — That equipment used downstream from the operational equipment to treat bleed water prior to disposal overboard. This equipment removes OIL from the WATER. Depending upon the same variables which effect the operation equipment, the effluent from the conditioning equipment will contain from 20 ppm to 200 ppm oil. Close observation is required in order to maintain an effluent in the 20 ppm to 50 ppm oil range. This is not always achieved.

Units which may be classified as conditioning equipment include:

1 Gravity separators.

2 Oil skimmers.

3 Clarifiers.

4 Gas flotation cells.

5 Coalescers.

This conditioning equipment can be installed at a cost of \$2 to \$3 per barrel or \$20,000 to \$30,000 for a system designed to process 10,000 barrels per day. This cost is based on the assumption that the equipment would be customized and designed to achieve an effluent of 50 ppm oil. This system would occupy about 300-400 sq. ft. and would require 3-4 months for delivery. The price would double if the equipment were installed after construction of the platform was completed.

Chemical treatment may be used to provide more consistent results in the 50 ppm oil range. This, however, generates a large amount of sludge which is a disposal problem in itself. Operating data indicate 30 to 500 lb/day ferric chloride would be needed to obtain 50 ppm oil. This would generate 4 cubic feet of sludge for each pound of chemical used.

Gravity separators, oil skimmers and clarifiers rely on the gravity separation of oil from water. Oil is normally skimmed off the top of these units and water is drawn from the bottom by way of an outside siphon called a "Gun Barrel". These units are normally used upstream from other oil removal equipment

to eliminate the bulk of free oil and sedimentation.

Gas flotation units saturate "clean" water with gas in a pressure tower. This water is then mixed with the water/oil mixture in a flotation chamber in which the gas bubbles expand and carry the oil particles to the surface where they are skimmed off. "Clean" water is then drawn off and discharged with a portion being recirculated to the gasification pressure tower. These units are capable of removing 90 percent of the oil from influents ranging as high as 1000 ppm oil.

In coalescer units the water/oil mixture enters a settling section where heavier solids fall out and free oil rises to the surface. The flow then travels through a graded filter bed or excelsior section where oil wetted particles are filtered out and finely dispersed oil particles are coalesced to particle size sufficient to rise out of the water. After filtering, the water passes to a final settling and surge section.

- C New proprietary equipment is being developed by several companies which, it is hoped, will reduce the amount of oil in the bleed water, and at the same time reduce the equipment space requirements. To date, this equipment has not been in service offshore but based on existing data, it is felt that effluent concentrations of 10 ppm to 25 ppm oil are achievable. The space requirements for these units range from

50 to 80 square feet, with cost estimates from \$20,000 to \$30,000 installed offshore.

III SUMMARY

By 1980 exploratory drilling and possibly production will be extended to coastal shores and slopes of about 120 countries. The estimated value during that year will be about \$14 billion and the cumulative value of offshore operations will be more than \$50 billion.

The offshore oil industry is expanding at a rapid pace and as the industry grows so does its associated pollution problems. Present equipment is capable of producing effluent bleed water with oil concentrations in the 50 to 200 ppm range. This conditioning equipment costs about \$2 to \$3 per barrel per day to install and requires 300-400 square feet of valuable platform space.

More efficient equipment is needed so that this industry can continue to grow without placing additional loads on an already overburdened environment.

Outline prepared by J. S. Dorrier, Acting Chief, Oil Research and Development Section, Edison Water Quality Laboratory, Edison, New Jersey 08817, January 1971.

BIOLOGICAL EFFECTS OF OIL POLLUTION

I INTRODUCTION

The suffering and mortality caused to birds by oil pollution, the coating of public and private property with layers of oil, is extremely conspicuous and attracts great public attention and sympathy. We hear conflicting statements from competent and respected scientists regarding the biological effects of these incidents. Why this divergence of opinion? Primarily, because data upon which to base a sound opinion is either incomplete, superficial or both.

II EVALUATING EFFECTS OF OIL

It is difficult to evaluate the effects of oil since it is not a single substance but a complicated and variable mixture of literally thousands of chemical compounds. This fact is clearly demonstrated in Table I (4) which shows that the toxicity of crude oils alone can cause mortality in the organism tested from as high as 89% to a low of 1%. These constituents of oil share many common properties; however they also differ considerably in many properties which influence their effects on the environment. Among these are:

1. Toxicity - Many low boiling aromatic hydrocarbons are lethal poisons to almost any organism while some higher boiling paraffin hydrocarbons are essentially non-toxic to most forms of life.

2. Solubility - Benzene derivatives may be soluble in water at concentrations around 100 ppm; naphthalenes at 30 ppm, while higher molecular

weight hydrocarbons may be essentially insoluble in water. Solubility, of course, will significantly influence the toxicity of a component of oil.

3. Biodegradability - This varies widely according to such molecular features as hydrocarbon chain length and degree of branching. The rate of degradation, of course, will influence the persistence of environmental effects.

4. Factors such as volatility, density, and surface-activity which will determine whether oil components or an oil mixture will tend to evaporate, sink, or easily disperse into the water column. Dean (1968) reports that two thirds of Nigerian and two fifths of Venezuelan crude oil will evaporate after a few days.

5. Carcinogenicity - Some components of crude, refined, and waste oils are known to have cancer-inducing properties.

III EFFECTS OF OIL

A General

Oil pollution, whether it be due to the spill or discharge of a crude oil or a refined product, may damage the marine environment many different ways, among which are:

1) Direct kill of organisms through coating and asphyxiation.

2) Direct kill through contact poisoning of organisms.

3) Direct kill through exposure to the water-soluble toxic components of oil at some distance in space and time from the accident.

4) Destruction of the food sources of higher species.

5) Destruction of the generally more sensitive juvenile forms of organisms.

6) Incorporation of sublethal amounts of oil and oil products into organisms resulting in reduced resistance to infection and other stresses (the principal cause of death in birds surviving the immediate exposure to oil.)

7) Destruction of food values through the incorporation of oil and oil products, into fisheries resources.

8) Incorporation of carcinogens into the marine food chain and human food sources.

9) Low level effects that may interrupt any of the numerous events necessary for the propagation of marine species and for the survival of those species which stand higher in the marine food web.

Because of their low density, relative to sea water, crude oil and distillates should float; however, both the experiences of the "Torrey Canyon" and of the "West Falmouth" oil spill have shown oil on the sea floor. Oil in inshore and offshore sediments is not readily biodegraded; it can move with the sediments and can contaminate unpolluted areas long after an accident.

B Waterfowl

Marine birds, especially diving birds, appear to be the most vulnerable of the living resources to the effects of oil spillage. Harm to the birds from contact with oil is reported to be the result of a breaking down of the natural insulating oils and waxes shielding the birds from water and loss of body heat, as well as due to plumage damage and ingestion of oil or an oil dispersant mixture. In addition, birds may be harmed indirectly through contamination of nesting grounds or through interruption of their food chain by destruction of marine life on which the birds feed.

The possible effects of the spillage on the bird population will vary with the season. For example, young birds during the late nesting season and flightless adults during the moulting season may be particularly vulnerable along the shore. Conversely, various groups of migratory birds may avoid exposure because of their absence at the time of the spill. Non-migratory birds will be the hardest hit with the possibility of eliminating an entire colony.

Bird kills in the thousands may result from a specific spill incident. Efforts to cleanse or rehabilitate contaminated birds have generally been unsuccessful with less than 20 percent of the treated birds surviving. Estimates of the ability of bird groups to repopulate differ greatly; however, there is a general consensus that the numbers of many marine bird types are vastly reduced from 30 years ago.

C Shellfish

Shellfish including mollusks such as clams, oysters and scallops along with crabs, lobsters, and shrimp appear to be the segment of marine life most directly affected by oil spillage in the coastal zone. Most of these types will survive contamination by heavy oil alone however the flavor of the flesh will be tainted. Lighter petroleum fractions such as diesel or gasoline appear to be more fatal, and some species such as clams may experience significant mortalities. Fortunately, in most spill incidents, the effects on shellfish appear to be fairly temporary, and even in those situations where high mortalities were observed at the time of the incident, recovery appears to have taken place within a period of six months to two years.

D Fish

Finfish generally appear to be unaffected by the presence of spilled oil as their mobility permits them to avoid areas with high oil or chemical concentrations. Danger to fish is probably limited to possible harm to eggs, larvae, or juveniles which seasonally may be found concentrated in the upper water layers or in shallow areas nearshore.

E Marine Mammals

Relatively few observations of any direct effect of oil spills on larger marine mammals such as whales, seals, and sea lions have been made. These animals appear to be able to sense and avoid oil on the surface of the water, and various accounts of oil-covered animals do not appear to be substantiated. Possible effects to young or disabled mammals are viewed as being comparable to normally occurring mortalities, and spilled oil is generally considered to result in minimal harm to marine mammals.

F Marshes

"Cowell reports that the short-term effect of oil on a marsh is that the oil adheres firmly to the plants and hardly any is washed off by the tide, except where there are puddles of oil. Leaves may remain green under the oil film for a few days, but eventually they become yellow and die. Plants recover by producing new shoots, a few of which can usually be seen within 3 weeks of pollution, unless large quantities of oil have soaked into the plant bases and soil. Seedlings and annuals rarely recover.

In the long term, recovery from oil spillages has been observed many times (e.g., Buck and Harrison, 1967; Ranwell, 1968; Stebbings, 1968; Cowell & Baker, 1969). The cases described cover different salt marsh communities, different types, volumes and degrees of weathering of oil, and pollution at different times of year. Vegetative recovery from experimental spraying at different times of year has been observed (Baker, 1970). The evidence indicates that marshes recover well from a single oil spillage, or from successive oil spillages provided these are separated by long time intervals."

G Food Chain

The effects of oil spillage on the marine food chain or food web (which consists of plants, bacteria and small marine organisms) is not well understood because of the wide fluctuations and cycles that occur naturally and are totally independent of the effects of oil. Lower marine plants appear to be fairly tolerant to contamination by oil & where destruction has taken place, have repopulated rapidly although in proportions varying from original numbers. Some forms of algae and diatoms appear to be stimulated in growth by a certain amount of oil. Various bacterial organisms will also feed on available oil and multiply, thus, providing energy to the protozoan level of the food chain. In general, based on today's knowledge, oil spillage does not appear to have lasting effects on the food elements of the marine environment.

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This outline prepared by R. T. Dewling,
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January 1971.

TABLE I - Chemical and physical properties of crude oils 1-10 with figures of relative toxicity at different temperatures. (4)

	1	2	3	4	5	6	7	8	9	10
Specific Gravity at 16°C/16°C	0.797	0.843	0.794	0.876	0.851	0.869	0.854	0.89	0.851	0.971
Sulphur Content %wt.	0.05	0.20	<0.1	0.96	1.7	2.5	1.33	0.96	0.75	2.59
Asphaltenes Content %wt.	<0.05	<0.05	NIL	2.8	0.5	1.4	0.7	0.17	0.7	5.8
Pour Point °C	27	9	13.5	7	6	-32	-21	-1	7	'15
Wax content %wt.	-	5.1	-	19.07	8.2	17.0	8.6	28.9	12.4	3495
Viscosity at 21°C cSt	2.34	3.0	1.65	8.32	5.5	9.6	5.6	13.4	6.45	739
Viscosity at 38°C cSt	26.7	20.1	36.2	14.6	17.3	15.3	17.9	10.7	26.3	2.8
Total distillate to 149°C %wt.	42.7	37.2	53.2	26.8	31.5	27.6	32.3	21.8	39.9	7.0
Total distillate to 232°C %wt.	69.7	67.5	75.6	48.3	51.7	44.6	52.5	43.5	60.5	22.7
Total distillate to 343°C %wt.	75.8	72.5	79.8	53.6	56.4	48.7	57.4	48.4	65.1	27.4
Total distillate to 371°C %wt.	0.744	0.749	0.731	0.737	0.705	0.703	0.718	0.742	0.717	0.736
S.G. at 16°C/16°C of C ₅ -149°C Cut	0.842	0.924	0.889	0.961	0.957	0.975	0.958	0.961	0.933	1.013
S.G. at 16°C/16°C of C ₅ -371°C Residue	13.5	10	17	17	8	7	7.5	18.5	13	10
Aromatic content of C ₅ -149°C Cut %wt.	45	47	24	55	82	71	76	79	7	66
% Mortality in <u>L. littoralis</u> * at 3°C	89	74	83	63	56	72	48	32	21	1
% Mortality in <u>L. littoralis</u> at 16°C	66	47	60	38	56	45	62	53	15	2
% Mortality in <u>L. littoralis</u> at 26°C										

*Intertidal Gastropods

LEGAL RESPONSE

Legislation Affecting Oil Pollution

National and Regional Contingency Plans

Functions, Responsibilities, and Role of On-Scene Commander

LEGISLATION AFFECTING OIL POLLUTION

I INTRODUCTION

On April 3, 1970, the President of the United States signed into law the "Water Quality Improvement Act of 1970". This is the latest law enacted to fight oil pollution. It is one of many laws passed to combat oil spills since the first oil well was drilled in the United States in Titusville, Pennsylvania on August 27, 1859.

II PRIOR LAWS

A "Refuse Act"

U. S. Code, Title 33, Section 407 Law enacted by Congress in March 1899. Superseded prior act of September 19, 1890. This act not only forbids discharge of refuse into the navigable waters, it also forbids the placing of refuse on the banks of a navigable water, where such refuse shall be liable to be washed into the navigable water. The penalty under this section is covered by Section 411 and provides for a fine not exceeding \$2,500 nor less than \$500, or by imprisonment (in the case of a natural person) for not less than thirty days nor more than one year, or by both such fine and imprisonment, in the discretion of the court, one-half of such fine to be paid to the person or persons giving information which shall lead to conviction.

B U. S. Code Title 33, Section 441 Law enacted by Congress on June

29, 1888. Superseded prior to act of August 5, 1886. This act is known as "The Supervisor of New York Harbor Act", but it also applies to the harbors of Baltimore, Maryland and Norfolk, Virginia. This act provides, upon conviction, a person shall be punished by fine or imprisonment, or both, such fine to be not less than \$250 nor more than \$2,500, and the imprisonment to be not less than thirty days nor more than one year, either or both united, as the judge before whom conviction is obtained shall decide, one half of said fine to be paid to the person or persons giving information which shall lead to conviction of this misdemeanor.

C U. S. Code Title 33, Section 433 Law enacted by Congress on June 7, 1924. This law was superseded by the Federal Water Pollution Control Act of 1965-66.

D Outer Continental Shelf Land Act of 1953 U. S. Code Title 43. The Outer Continental Shelf Land Act of August 7, 1953, among other things, authorizes the Secretary of the Interior to issue on a competitive basis leases for

oil and gas, sulphur and other minerals in submerged lands of the Outer Continental Shelf, as defined in section two of the act. Subject to the supervisory authority of the Secretary, the regulations shall be administered by the Director, Bureau of Land Management.

- E U. S. Code Title 33, Section 1001 enacted by Congress in 1961. Public Law 87-167 (International Convention on Prevention of the Sea by Oil). To prevent discharge or escape of oily substance by sea-going vessels (NOTE: Oily substance is defined as persistent oil). Vessels required to maintain Oil Record Book. Prohibited zone: All seas within 50 miles from nearest land (baseline from which territorial sea is established) and other areas as defined in the convention.

- F Federal Water Pollution Control Act of 1965-66. U. S. Code Title 33, Section 466. This act superseded the Oil Pollution Act of 1924. This was not a strong law because to obtain a conviction under this act you had to prove "intent", or gross negligence.

III. WATER QUALITY IMPROVEMENT ACT OF 1970. PUBLIC LAW 91-224

A Section II Control of Pollution by Oil

- 1 Quantities of oil which may be discharged

The Federal Register, Volume 35, #177 dated September 11,

1970, gives this definition of oil which may not be discharged: Include discharge which:

- a Violate applicable water quality standards, or
- b Cause a film or sheen upon or discoloration of the water or adjoining shorelines or causes a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.

2 Notification (Penalty)

The Federal Register, Volume 35, #227 dated November 21, 1970, states: Subsection 11(b)(4) of the Act requires that any person in charge of a vessel or of an onshore or offshore facility, as soon as he has knowledge of any discharge of oil in harmful quantities from such vessel or facility into or upon the waters designated by the Act or the adjoining shorelines, shall immediately notify the appropriate agency of the United States Government of such discharge. The "appropriate agency" is listed as follows:

- a The Commanding Officer or officer in charge of any Coast Guard unit in the vicinity of the discharge;
- b The Commander of the

Coast Guard District in which the discharge occurs.

- c The Federal official designated in the Regional Oil and Hazardous Materials Pollution Contingency Plan as the On-Scene Commander (OSC) for spill response purposes.
 - d The Commandant, U. S. Coast Guard.
 - e Regional Director, EPA Water Quality Office, for the region in which the discharge occurs. The penalty for failure to notify one of the foregoing immediately is \$10,000.
- 3 Knowingly discharging oil (Penalty)

Section 11(b)(5) of the Act provides \$10,000 fine for knowingly discharging oil into the navigable waters. This is a civil penalty and shall be assessed by the Secretary of the department in which the Coast Guard is operating. Each violation is a separate offense.

4 Areas affected

The discharge of oil into or upon the navigable waters of the United States, adjoining shorelines, or into or upon the waters of the contiguous zone in harmful quantities, as determined by the President,

is prohibited, except (A) in the case of such discharges into the waters of the contiguous zone, where permitted under Article IV of the International Convention for the Prevention of the Sea by Oil, 1954, as amended and (B) where permitted in quantities and at times and locations or under such circumstances or conditions as the President may, by regulation, determine not to be harmful.

5 Removal of oil from water and shoreline

Whenever any oil is discharged, into or upon the navigable waters of the United States, adjoining shorelines, or into or upon the waters of the contiguous zone, the President is authorized to act to remove or arrange for the removal of such oil at any time, unless he determines such removal will be done properly by the owner or operator of the vessel, onshore facility, or offshore facility from which the discharge occurs.

6 Strike force

Section 11(c)(2)(c) of the Act, states, "establishment or designation of a strike force consisting of

personnel who shall be trained, prepared, and available to provide necessary services to carry out the Plan, including the establishment at major ports, to be determined by the President, of emergency task forces of trained personnel, adequate oil pollution control equipment and material and a detailed oil pollution prevention and removal plan".

7 Dispersants and other chemicals

Dispersants shall not be used:

- a On any distillate fuel.
- b On any spill of oil less than 200 barrels in quantity.
- c On any shoreline.
- d In any waters less than 100 feet deep.
- e In any waters containing major populations, or breeding or passage areas for species of fish or marine life which may be damaged or rendered commercially less marketable by exposure to dispersant or dispersed oil.
- f In any waters where winds and/or currents are of such velocity and directions that dispersed oil mixtures would likely, in the judgment of EPA, be carried to shore areas within 24 hours.

- g In any waters where such use may affect surface water supplies.

8 Sinking agents

Sinking agents may be used only in waters exceeding 100 meters in depth where currents are not predominantly on-shore, and only if other control methods are judged by EPA to be inadequate or not feasible.

9 Removal or destruction of vessel

Because of a discharge, or an imminent discharge, of large quantities of oil from a vessel, the United States may (A) coordinate and direct all public and private efforts directed at the removal or elimination of such threat; and (B) summarily remove, and, if necessary, destroy such vessel by whatever means are available without regard to any provisions of law governing the employment of personnel or the expenditure of appropriated funds.

10 Cost of cleanup

a Vessel

An owner or operator of a vessel from which oil is spilled, shall be liable to the United States Government

in an amount not to exceed \$100 per gross ton of such vessel or \$14,000,000, whichever is lesser, except that where the United States can show that such discharge was the result of negligence or willful misconduct within the privity and knowledge of the owner, such owner or operator shall be liable to the United States Government for the full amount of such cost. Such cost shall constitute a maritime lien on such vessel which may be recovered by an action in rem in the district court of the United States for any district within which any vessel may be found.

b Offshore facility

The owner or operator of offshore facility from which oil is spilled, shall be liable to the United States Government for the actual cost incurred for the removal of such oil by the United States Government in an amount not to exceed \$8,000,000, except that where the United States can show that such discharge was the result of willful negligence or willful misconduct within the privity and knowledge of the owner, such owner or operator shall be liable to the United States Government for the full amount of such cost. The United States Government

may bring an action against the owner or operator of such a facility in any court of competent jurisdiction to recover such cost.

c Onshore facility

The owner or operator of an onshore facility from which oil is spilled shall be liable to the United States Government for the actual cost incurred for the removal of such oil by the United States Government in an amount not to exceed \$8,000,000, except that where the United States can show that such discharge was the result of willful negligence or willful misconduct within the privity and knowledge of the owner, such owner or operator shall be liable to the United States Government for the full amount of such cost. The United States may bring an action against the owner or operator of such facility in any court of competent jurisdiction to recover such cost.

11 Revolving fund

The provisions of Public Law 91-224 authorizes to be appropriated a revolving fund to be established by the Treasury not to exceed

\$35,000,000 to carry out the provision of cleanup as stated by the act. Any other funds received by the United States under this Act shall also be deposited in said fund for such purposes. All sums appropriated to, or deposited in, said fund shall remain available until expended.

12 Evidence of financial responsibility

Public Law 91-224 provides that any vessel over three hundred gross tons, including any barge of equivalent size, using any port or place in the United States or the navigable waters of the United States for any purpose shall establish and maintain under regulations to be prescribed from time to time by the President, evidence of financial responsibility of \$100 per gross ton, or \$14,000,000 whichever is the lesser, to meet the liability to the United States which such vessel could be subjected under this law. In cases where an owner or operator owns, operates, or charters more than one such vessel, financial responsibility need only be established to meet the maximum liability to which the largest of such vessels could be subjected. Financial responsibility may be established by any

one of, or a combination of, the following methods acceptable to the President: (A) evidence of insurance; (B) surety bond; (C) qualification as a self-insurer; or (D) other evidence of financial responsibility. Any bond filed shall be issued by a bonding company authorized to do business in the United States.

Outline prepared by Howard
Lamp'1, Contingency Plans
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08817, January 1971.

NATIONAL AND REGIONAL CONTINGENCY PLANS

I INTRODUCTION

The Federal Water Pollution Control Act, as amended (P.L. 91-224, 84 Stat. 93, 1970) directed the preparation of a National Contingency Plan for Oil and Hazardous Materials. This plan was published in the Federal Register on June 2, 1970. It superseded the National Multiagency Oil and Hazardous Materials Contingency Plan which was approved in September, 1968.

II PURPOSE

The Plan represents an agreement among concerned departments and agencies of the federal government for a pattern of coordinated and integrated response to major pollution incidents. It establishes a national response team and provided guidelines for the establishment of regional contingency plans and response teams. The plan promotes the coordination and direction of federal, state and local response systems and encourages the development of local government and private capabilities to handle such pollution incidents.

III OBJECTIVES

The objectives of the plan are to develop effective systems for discovering and reporting the existence of a pollution incident, promptly instituting measures to restrict the further spread of the pollutant, to assure that the public health, welfare and national resources are provided adequate protection, application of techniques to clean up and dispose of the collected pollu-

tants, and institution of action to recover clean up and effective enforcement of existing federal statutes.

IV SCOPE

The plan is effective for all United States navigable waters including inland rivers, the Great Lakes, coastal territorial waters, and the contiguous zone and high seas beyond this zone where there exists a threat to United States waters, shoreface or shelf bottom.

V PARTICIPATING AGENCIES

Each of the primary Federal agencies has responsibilities established by statute, Executive Order or Presidential Directive, which may bear on the Federal response to a pollution incident. This plan intends to promote the expeditious and harmonious discharge of these responsibilities through the recognition of authority for action by those agencies having the most appropriate capability to act in each specific situation.

The primary Federal Agencies are the Environmental Protection Agency, the Departments of Transportation, Defense and Health, Education and Welfare and the Office of Emergency Preparedness.

VI ORGANIZATION

The plan calls for the establishment of a National Inter-Agency Committee (NIC) which is the principal instrumentality for plans and policies of the federal multi-agency response to pollution emergencies.

At the Washington level, the plan establishes a National Response Team (NRT) which consists of representatives of the signatory agencies which shall act as an emergency response team to be activated in the event of a pollution incident involving oil or other hazardous material which: (a) exceeds the response capability of the region in which it occurs, (b) transects regional boundaries, or (c) involves national security or major hazard to substantial numbers of persons or nationally significant amounts of property. A National Response Center (NRC) in Washington, D.C. is the headquarters site for activities relative to pollution incidents.

There are established throughout the United States, Regional Response Teams (RRT) that perform functions within the local regions similar to that performed by the National Response Team on the national level. Regional Response Centers (RRC), similar to the NRC, are located in each of the pre-designated regions.

The plan further provides that in each region, there will be established On-Scene-Commanders (OSC). The On-Scene-Commander is the single executive agent pre-designated by regional plan to coordinate and direct such pollution control activities in each area of the region.

VII DELEGATION OF RESPONSIBILITY

The U. S. Coast Guard is to provide for On-Scene-Commander's in areas where they have assigned responsi-

bility, which includes the high seas, coastal and contiguous zone waters, coastal and Great Lakes ports and harbors. The Environmental Protection Agency will furnish or provide for On-Scene Commander's in other areas.

VIII FEDERAL RESPONSE OPERATION

The actions taken to respond to a spill or pollution incident can be separated into five relatively distinct classes or phases. For descriptive purposes, these are:

Phase I. Discovery and Notification;

Phase II. Containment and Counter-measures;

Phase III. Cleanup and Disposal;

Phase IV. Restoration;

Phase V. Recovery of Damages and Enforcement.

It must be recognized that elements of any one phase may take place concurrently with one or more other phases.

IX REGIONAL CONTINGENCY PLANS

Separate regional plans are to be developed by the Environmental Protection Agency and the United States Coast Guard for the respective areas of responsibility within each region. All regional plans are to be oriented in accordance with the ten (10) standard federal administration regions.

All regional contingency plans will contain, as a minimum the following items:

- A. A definition of the area covered including the points of change in jurisdiction between Environmental Protection Agency and U. S. Coast Guard.
- B. A notification and reporting system beginning with the initial discovery of an incident.
- C. Names, addresses and phone numbers of all pertinent federal, state, local and industry personnel involved in the reporting system.
- D. A listing of predesignated On-Scene Commander's and Regional Response Center's.
- E. Listing of resources and equipment available in the regional area with names, addresses and phone numbers.

This outline was prepared by A. W. Bromberg, Chief, Operations Branch
FWQA, Edison Water Quality Laboratory

FUNCTIONS, RESPONSIBILITIES AND ROLE OF THE ON-SCENE -COMMANDER

I INTRODUCTION

- A You may be designated as the On-Scene-Commander during the next major oil spill that takes place in your area of responsibility. Are you prepared?

II BACKGROUND

- A What are the qualifications of a good On-Scene-Commander? He should be a well trained individual, whose background includes oil pollution research, experience with a number of actual spills of different types of oil, a knowledge of the shipping industry and a good background in law and existing oil pollution legislation.
- B Basically, the On-Scene-Commander is a decision making "machine", working at least twelve hours per day over a long period of time. To make these decisions in an intelligent manner, he must have the basic background to support his decisions. If a wrong decision is made, the results could range from embarrassment to the Federal Government, to injury or death to substantial numbers of persons.
- C A good On-Scene-Commander must have many attributes. First of all, he must have good managerial ability. From utter chaos, he must organize a small army of men and equipment to remove the oil from the water and shore-face. He must be a statistician for he has to provide and direct great amounts of money, equipment

services and manpower. He must have a sense of humor, because no matter how well the cleanup is going, some elements of the public are going to cry for instant and dramatic cleanup. And finally, he must have the ability to walk a tenuous tightrope, to try to please as many of the public, who have been injured by the spill, as possible. For instance: the sunbathers and swimmers want the beaches and surf cleaned at once; the bird lovers want the birds protected at all cost; the vessel owner wants his vessel cleaned of all traces of oil pollution; shore-front property owners want their homes protected and cleaned; the commercial and sports fishermen would rather have the oil come ashore than have it to any damage to marine life; and finally, the oil and shipping industry want the channels kept open at all cost.

III ORGANIZATION

A Staff

Every On-Scene-Commander should be backed up with a fully trained staff. This staff should include, but is not limited to: a public information officer, to handle the countless calls and inquiries from the news media; a stenographer, to keep a running account of all business transacted during any given day; a

contracting officer, to handle the myriad details for the hiring of and negotiations with various contractors, purchase request and the recording and handling of petty cash funds. He should also have on his staff, technicians to supervise and "straw-boss" the various contractors and to do general field work during the life of the spill. These technicians should be well versed in oil pollution work. Finally, the On-Scene-Commander should have available to him legal council for consultation when the need arises; fully trained chemist, biologist and engineers who have a good background in oil pollution work.

B Quarters and Equipment

The On-Scene-Commander and his staff should have a suitable headquarters in which to work. Ideally, a Coast Guard Station would provide a suitable headquarters if it were near the scene of the spill. If not, then other quarters must be found. These quarters could be a suite of motel or hotel rooms; a house trailer; a mobile laboratory, as found in the EPA, Water Quality Offices, or a private beach house.

The operations headquarters should be equipped with the following items: wall charts; maps; at least eight telephones; desks; chairs; writing equipment; typewriters and if possible, a teletypewriter. One of the most important items of equipment in the headquarters, is the Commander's Log. The Commander's Log, a permanent bound book, should

be maintained from the inception of the spill until the case is closed out. In it, there should be recorded, chronologically, a reference to all telephone calls received, meetings held, orders issued, events taking place, personnel changes, visitors received, overflights made, etc. This Log can be an invaluable record of the spill to be later used in court or congressional hearing.

C Communications

Whenever the On-Scene-Commander and his staff are housed, the first order of business upon arrival is to order phones. At least eight phones should be installed. One of the eight telephone numbers should not be given out for general use, but should be reserved and made known to only a few selected individuals who may have to communicate with the On-Scene-Commander on urgent matters.

It is imperative that the On-Scene-Commander have communications with the contractors in the field and with his observers. Small, portable hand-held radios with sufficient range would be the ideal answer. If radio communications are not available, there is another system which can be found in most large cities. This system is called "People Beepers". It is a small, belt-clip-on radio receiver with a range of approximately twenty-five miles. To get a contractor or observer in

the field, the On-Scene-Commander dials a specified number and asks the operator to have No. A-16 call headquarters. The operator in turn activates a "beeper" on the radio receiver No. A-16 and transmits the message. The holder of receiver No. A-16 in turn calls the On-Scene-Commander by telephone and communications are established. This system can be rented for a nominal fee.

Communications between air observers and headquarters is a necessity and observation and work vessels should also be able to contact the field headquarters.

IV RELATIONS WITH OTHER ORGANIZATIONS

A Federal

- 1 Environmental Protection Agency
- 2 U. S. Coast Guard
- 3 U. S. Army Corp of Engineers
- 4 U. S. Health, Education and Welfare
- 5 Office of Emergency Preparedness

These are the basic Federal Agencies concerned with a major oil spill. However, many other Federal Agencies may be called on to furnish help during the life of the emergency; they may include, but are not limited to, the following:

- a U. S. Air Force
- b U. S. Navy
- c U. S. Army
- d General Accounting Office
- e General Services Administration

B States

Individual states are encouraged to make commitments to the cleanup of major oil spills. If the state decides that it wants to take complete charge of the spill, it is the policy of the federal government to agree and then monitor the situation. The problem here lies in the fact that very few states have the funds committed by legislation to become involved in a major oil spill cleanup.

C Interstate Agencies

Interstate agencies too, are encouraged to make commitments to the cleanup of major oil spills. Interstate agencies can also take complete charge of a major oil spill, but again, the funding limitations applies to these agencies as well as to the individual states.

D Local Government

Local governments will rarely have the funds to combat a major oil spill. However, they can be an invaluable source of manpower and equipment.

E Academic Communities

The academic communities throughout the country can usually be counted on to furnish information and advice on the local environment, during a major spill. Quite often, you will find that these institutes have previously made extensive biological studies of local areas and this can be of invaluable help in comparison with post spill biological surveys.

V FINANCING

A All cost of cleanup should be borne by the polluter. In most cases, the major oil and shipping companies will shoulder this responsibility without question. If the company agrees to finance the cost of cleanup, they will probably want to take charge of the operations. This is agreeable to the federal government—however, the On-Scene-Commander and his staff should monitor the complete cleanup operation. Should progress of the cleanup be not to the satisfaction of the On-Scene-Commander, he has the authority to make the company stop its operations and have the federal government proceed with the cleanup. All cost borne by the federal government will be reimbursed by the polluter.

B The individual state government can assume command of a spill cleanup, if they so desire. But again, the federal government's On-Scene-Commander must monitor all

phases of the cleanup. The states in turn can recover expended funds either through the individual state courts or the monies can be recovered through the federal courts.

C The federal government has established a thirty-five million dollar revolving fund for the cleanup of oil and other hazardous materials. This fund is administered by the U. S. Coast Guard. All monies expended by the federal government in the cleanup process, will be recovered from the polluter, either voluntarily or through the federal court system.

VI INDEPENDENT CONTRACTORS FOR CLEANUP

A Prior to the Torrey Caynon incident, it was very difficult to find a contractor who had the knowledge of oil spill cleanup or the desire to cleanup massive spills of oil. However, since that date, a new industry has evolved - the so-called "third party contractor" for the cleanup of oil spills.

B As mentioned previously, the On-Scene-Commander should have on his staff a responsible contracting officer. The contracting officer should handle all the details of the contract, payment and the keeping of complete records pertaining to all monies expended during the life of the spill. The On-Scene-Commander and the contracting officer should keep in mind that all paper work involved in cleanup cost will probably

end up as evidence in a federal court.

- C Prior to a major spill, a good On-Scene-Commander should have knowledge of all "third party" contractors in his area of responsibility. The On-Scene-Commander should know the people he is going to be working with during an emergency. He should know the amount of equipment the contractor has on hand, the type of equipment, the conditions of the equipment. He should know if the contractor has trained personnel or does he recruit from the streets. All this knowledge is important to the On-Scene-Commander, for he has to rely heavily on his working contractors.
- D Finally, the On-Scene-Commander should have available to him trained personnel to monitor the work of the various contractors in the field. This is necessary to insure that the federal government receives full value for every dollar spent on the cleanup.

VII REPORTS REQUIRED

- A The National Contingency Plan requires that the On-Scene-Commander submit two situation reports daily. One at 0800 hours and one at 2000 hours. These reports are normally submitted by teletype. If any event of dramatic importance occurs at other times of the day, the National Response Team should be notified by teletype at once.
- B When the emergency is over, and the Regional Response Team is

disbanded, the On-Scene-Commander should prepare his "End of Operations" report. This report should contain as much information as possible about the entire life of the spill incident. The Commander's Log will prove invaluable to the On-Scene-Commander's preparation of his report. Once completed, the report should be forwarded to the National Response Team through the Regional Response Team.

This outline was prepared by H. J. Lamp'l, Contingency Plans Officer, FWQA, Edison Water Quality Laboratory

OIL CHARACTERISTICS

Chemical and Physical Characteristics

Fate and Behavior

Oil Sampling

Oil Identification

PHYSICAL AND CHEMICAL CHARACTERISTICS OF OIL

I PHYSICAL CHARACTERISTICS OF OIL

A Introduction

Crude oil varies in color from black through various shades of brown and green to a light yellow. It may be heavy and viscous such as Bachaquero crude oil from Venezuela or light and volatile such as South Louisiana crude oil. The main physical properties used to characterize an oil are its specific gravity, API (American Petroleum Institute) viscosity, pour point, flash point, cloud point and ash content.

B Physical Properties

- 1 Specific gravity is the ratio of the density of an oil to the density of water when both are measured at a given temperature:

$$s = \frac{d_o}{d_w}$$

Where s is the specific gravity, d_o is the density (mass per unit volume) of the oil, and d_w is the density of water (1.000 g/ml at 3.98° C).

- 2 API gravity is defined by the following equation:

$$\text{API gravity} = \frac{141.5}{s_{60^\circ F}} - 131.5$$

where $s_{60^\circ F}$ is the specific gravity of the oil at 60° F.

- 3 Viscosity is defined as the resistance to flow.

- a Absolute viscosity is the force required to move a plane surface area of one square centimeter over another plane surface at the rate of one centimeter per second when the two surfaces are separated by a layer of liquid one centimeter in thickness.

- b Kinematic viscosity is the ratio of the absolute viscosity to the specific gravity of the oil at the temperature at which the viscosity is measured.

- 4 Pour Point is the lowest temperature at which the oil will flow.

- 5 Flash Point of an oil is the temperature at which it gives off sufficient flammable vapor to ignite. This should not be confused with the fire point of an oil which is the temperature at which its vapors will continue to burn. The fire point of an oil ranges from 10° to 70° higher than its flash point.

- 6 Cloud Point is the tempera-

ture at which the paraffins of an oil, which are usually in solution begin to crystallize causing the oil to become cloudy.

- 7 Ash Content is the amount of noncombustible material in an oil.
- 8 Other Properties: Many other properties are also noted for specific types of petroleum products. For example, octane number is determined for gasoline, and viscosity index, an empirical number indicating the effect of a change in the temperature on the viscosity, is determined for lubricating oils.

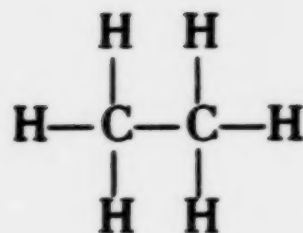
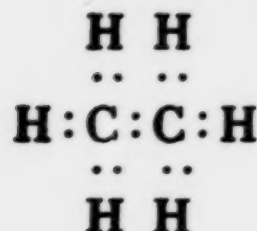
II CHEMICAL COMPOSITION OF OIL

A Introduction

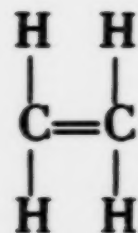
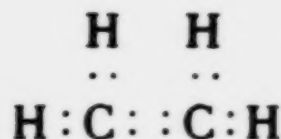
Another method of classifying petroleum products is according to the types of chemical compounds which it contains. For convenience, a group of definitions is included.

B Definition of Terms

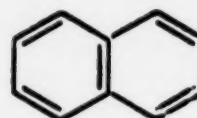
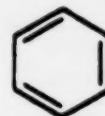
- 1 Hydrocarbon is a chemical compound which contains only the elements carbon and hydrogen.
- 2 Saturated Hydrocarbons are hydrocarbons which have only single bonds.
- 3 A Single Bond is formed when two valence electrons are shared by two atoms.



- 4 A Double Bond is formed when four valence electrons are shared by two atoms.



- 5 A Triple Bond is formed when six valance electrons are shared by two atoms.



- 6 An Unsaturated Hydrocarbon is one which contains one or more double or single bonds. The term unsaturated refers to the fact that hydrogen atoms are deficient and can be added under the proper chemical and physical conditions. Thus, ethylene and acetylene shown in 4 and 5 above, respectively, are unsaturated hydrocarbons.
- 7 An Aromatic Hydrocarbon is one which contains at least one 6-membered ring of carbon atoms and alternate single and double bonds. Benzene and naphthalene are therefore aromatic hydrocarbons.

C Chemical Composition of Crude Oils

1 Background

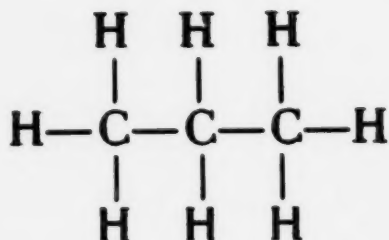
Crude oils vary greatly in composition but consist mainly of hydrocarbons and compounds containing oxygen, nitrogen, sulfur and trace amounts of metals in addition to carbon and hydrogen.

- 2 Hydrocarbons are the main class of compounds present in most crude oils. The range, however, is a wide one. Many mid-continent and Gulf of Mexico crude oils contain 90-95% hydrocarbons while crude oils

of Mexico and California have only 50% hydrocarbons. The hydrocarbon compounds in crude oil consist mainly of paraffins, napthenes, and aromatics.

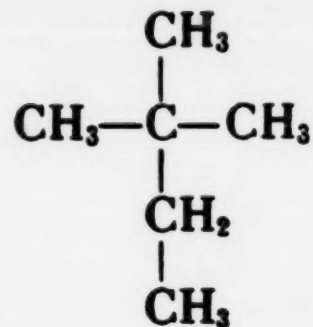
- a Paraffins are saturated hydrocarbons such as ethane. A wide range of paraffins can be found in crude oils. The light ends, the volatile components are mainly low molecular weight paraffins containing 12 or less carbons.

- 1 Straight-Chain Paraffins are those in which the carbon atoms are arranged linearly.

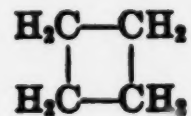


- 2 Branched-Chain Paraffins are those which have a linear arrangement of carbon atoms with other carbon atoms attached to

the carbons of the main chain.



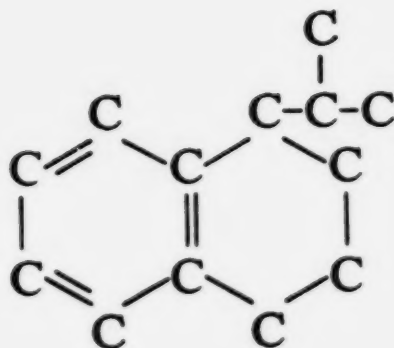
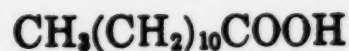
- b Napthenes are cycloparaffins. That is, the two ends of an open chain are joined together, forming a cyclic structure.



The cyclo-paraffins of crude oils consist almost entirely of cyclopentane and cyclohexane rings with or without straight or branched-chain paraffin groups attached to the ring.

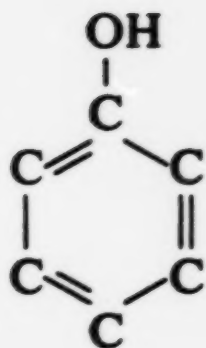
- c Aromatics in crude oils are found to a lesser degree than paraffins or cyclo-paraffins. They are usually found in the higher boiling fractions since they are for the most part of rather high molecular weight.
- d Other Hydrocarbons consist of combinations of the above three classes. For example, in the high boiling fractions naphthene rings may be fused to aromatics with side paraffin chains attached.

- 3 Oxygen-Containing Compounds in crudes are almost exclusively acid in nature. Fatty acids, naphthenic acids, and phenols have been found in very small amounts in most crudes, but naphthenic acids compose as high as 3% in some Russian (Baku) and Rumanian crudes. California crudes have as high as .5% naphthenic acids in contrast to the trace amounts found in other USA crudes. Fatty acids are paraffins with a terminal $-\text{COOH}$ group.



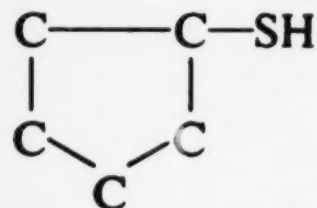
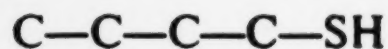
- 4 Naphthenic Acids are cyclo-paraffins with a $-\text{COOH}$ group attached.

- 5 Phenols are aromatic compounds with an OH group attached.



been identified as mercaptans (thiols) and sulfides. These can be either cyclic, or non-cyclic or a combination.

- 1 Mercaptans are paraffins, naphthene, and aromatics with -S-H groups attached.



6 Sulfur Containing Compounds

- a Crude oils vary in sulfur content from 0.1% in non-asphaltic Pennsylvania crudes to as high as 5% in some heavy, asphaltic crudes of California and Mexico. The identity of the sulfur compounds in the high boiling fractions are not known but those in the low boiling fractions have

- 2 Sulfides are compounds where an S atom replaces a non-terminal carbon atom.

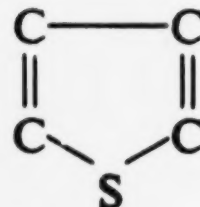
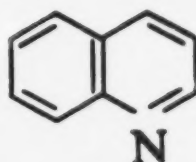
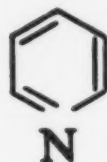


TABLE I
CRUDE OIL - CLASSIFICATION BY CONTENTS

Paraffinic
 Napthenic
 Paraffinic - Napthenic
 Paraffinic - Napthenic - Aromatic
 Napthenic - Aromatic
 Napthenic - Aromatic - Asphaltic
 Aromatic - Asphaltic

TABLE II		
<u>PRODUCT</u>	<u>BP RANGE</u>	<u>CARBON ATOMS</u>
LPG	-45° to 0.5° C	3 - 4
Light Gasoline	-.5° to 150°	4 - 9
Naptha	150° to 210°	9 - 12
Kerosene	151° to 270°	9 - 16
#1 Fuel Oil	210° to 330°	12 - 20
Gas Oil	216 to 343	15 - 20
Lube Oils Residuum		> 15 - 20
#2 Fuel Oil	225° to 360°	12 - 24
#4 Fuel Oil Heavy straight run or distillate		
#5 Fuel Oil Heavy straight run or cracked residual		
#6 Fuel Oil Heavier residuum		

- 3 Nitrogen Containing Compounds are found in only ver small proportions and consist mainly of quinoline and pyridine derivatives.



- 4 Trace Metal Compounds are a very important small component of crude oils. Vanadium, nickel, and iron compounds are among the most prominent. These metals are usually present as organometallic chelates.
- D Classes of Crude Oils are based on the relative compositions with respect to paraffinic, napthenic, aromatic, and asphaltic content. The main types are shown in Table 1.
- E Characteristics of Refined Petroleum Products
- 1 Boiling Ranges: Petroleum products are usually classified

according to their boiling ranges. The most common petroleum products, their boiling ranges, and approximate molecular weight ranges are listed in Table II.

Outline prepared by J. P. Laforanara, Research Chemist, Edison Water Quality Laboratory, Edison, New Jersey January 1971.

FATE AND BEHAVIOR OF SPILLED OIL

I INTRODUCTION

The tar-asphalt residue of the "weathering" of oil is a product of a complicated multi-process phenomenon. The main processes in roughly the order of occurrence after a spill are spreading, evaporation, dissolution and emulsification, auto-oxidation, microbiological degradation, sinking and resurfacing after which the process repeats itself. While these processes are occurring, the slick may also be moving.

II MAJOR PROCESSES IN THE DEGRADATION OF OIL

A Spreading

This process, the first to occur, thins the slick out to a few millimeters or less and is dependent on several parameters — among them, viscosity of the oil, surface tension of the oil and water, and time.

B Evaporation

Evaporation is the process by which the low molecular weight compounds of relatively low boiling point are volatilized into the atmosphere. The rate of this process is also governed by many parameters — among them, are viscosity of the oil, type of oil, and weather conditions, such as wind and sea state. The major loss due to evaporation occurs during the first few days.

C Dissolution

Dissolution is the process by which the low molecular weight compounds and polar compounds are lost by the oil to the large volume of water

under and around it. The rate of this process is also governed by many parameters including the type of oil, viscosity of the oil, the amount of oxidation the oil has undergone before, during and after the spill and the weather conditions such as wind, and sea state. Although this process starts immediately, it is a long term one and continues throughout the duration of the total weathering process since the oxidation and microbiological degradation processes constantly produce polar compounds which are finally dissolved in the water.

D Emulsification

Emulsification is the process by which one liquid is dispersed into another immiscible liquid in droplets of optically measurable size. In the case of oil, the emulsion can be either an oil-in-water emulsion or a water-in-oil emulsion.

E Auto-Oxidation

Auto-oxidation is the light catalyzed reaction by which hydrocarbons react with atmospheric oxygen to form ketones, aldehydes, alcohols and carboxylic acids which are all polar compounds which can either dissolve in the water or act as emulsifying agents or detergents.

F Microbiological Degradation

Microbiological degradation is a multi-faceted process. Certain bacteria, actinomycetes, filamentous fungi, and yeasts utilize hydrocarbons and chemically oxidized hydrocarbons as food sources.

1 Aerobic Microbial Oxidation

Most of the microorganisms which oxidize hydrocarbons require oxygen in either the free or dissolved form. When the oxidation of the oil occurs at the air-water interface there is usually sufficient oxygen to allow the maximum biological degradation to occur. However, areas of activity beneath the surface in the water column or in bottom muds are severely limited by the supply of oxygen.

2 Anaerobic Microbial Oxidation

A few organisms are known which oxidize hydrocarbons when little or no dissolved or free oxygen is present. These utilize nitrate or sulfate as their oxygen source. "Pseudomonas aeruginosa", for example, utilizes n-octane or n-hexadecane while reducing nitrate to nitrite. Many sulfate-reducing bacteria are known.

G Sinking

Evaporation, dissolution and oxidation of lighter hydrocarbons may cause the oil to increase its density. When this happens to a sufficient extent the oil will sink to the bottom where anaerobic microbial oxidation will be the main process of degradation.

H Resurfacing

If the density of the oil mass is reduced to a sufficient degree by anaerobic oxidation, the oil

will float again and the processes above will again occur until the oil has either completely disappeared or reaches some land mass.

III PHYSICAL MOVEMENT OF OIL SLICKS

In the absence of current or debris, an oil slick will move in the direction of the wind at a rate about 3-4 percent of the wind velocity. In the absence of wind or debris, an oil slick will move in the same direction with the same speed as the water current. The actual movement will be due to some combination of wind and current.

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This outline was prepared by Dr. J. Laforanara, Research Chemist, Edison Water Quality Laboratory, Edison, NJ January 1971.

OIL SAMPLING PROGRAM

I INTRODUCTION

- A A complete oil sampling program is undertaken for the primary purpose of presenting legal evidence in a court of law. To protect the interests of all parties concerned three basic sampling requirements should be observed:

- 1 The sample must represent that oil which was spilled.
- 2 The sample must not be physically or chemically altered by the collection procedure.
- 3 Transfer of the sample must be accomplished using a well defined chain of custody system.

- B The two basic types of oil sample analysis are:

- 1 Qualitative - to determine the presence or absence of oil and to compare the sample to a suspected source.
- 2 Quantitative - to determine the amount of oil present at the spill site.

Collection for qualitative analysis greatly exceeds collection for other purposes. For this reason, alternate methods are under study which will detect the presence of oil without the requirement for physical sampling. These methods will use photographic and electronic sensors and include:

- 1 Earthbound instrumentation.
- 2 Airborne instrumentation.

Earthbound instrumentation would be deployed in areas of high probability of spills such as in harbors and near terminals and refineries. Airborne instrumentation, on the other hand, would allow occasional spot checks of other areas and effective monitoring of cleanup operations. Ideally, such instrumentation should be capable of detection, identification and of providing aerial and thickness measurements.

Methods for tagging oils are also under study. These methods are grouped into two categories:

- 1 Active tagging
- 2 Passive tagging.

Active tagging requires that an inexpensive, coded material be added to oil. This material must be chemically and physically stable in both oil and oil slicks. It must be readily identifiable by available analytical techniques and it must have no adverse effect on the oil's subsequent use.

Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed by laboratory procedures.

Sampling for quantitative analysis is extremely difficult due to variations in slick thickness over the spill area. For this reason experienced, visual observation will generally provide more reliable information on the quantity of oil spilled. Table I is a guide for estimating the amount of oil on the water's surface.

II SAMPLE DETERMINATION

A The ideal sampling program is one in which collections are made BEFORE and AFTER the spill incident. The very nature of an oil spill, however, generally precludes "BEFORE" sampling.

B The types of samples to be collected depend on the following parameters:

1 Location of the spill.

a Offshore

b Harbor areas

c Inland waters

2 Uses of the area involved:

a Drinking water source

b Shellfish growing area

c Wildlife refuge

d Finfish spawning area

e Recreation

f Commercial fishing

3 Facilities available for analysis:

a Qualitative analysis

b Quantitative analysis

c No analysis

TABLE I

<u>Appearance of Slick</u>	<u>Amount of Oil</u>
Barely discernible	25 gal/sq. mi.
Silvery sheen	50 gal/sq. mi.
Faint colors	100 gal/sq. mi.
Bright bands of color	200 gal/sq. mi.
Dull brown	600 gal/sq. mi.
Dark brown	1,300 gal/sq. mi.

4 Source of spill

- a Offshore platform
- b Refinery
- c Terminal operation
- d Storm drain
- e Ship - in port
- offshore

C Qualitative analysis is performed to determine the presence (or absence) of a particular type of oil. This analysis may be performed on samples of:

- 1 Water
- 2 Fish and shellfish
- 3 Mud

In addition to direct chemical procedures, two additional types of qualitative analysis may also be performed to detect the presence of oil in water, fish and shellfish samples:

- 1 Taste tests
- 2 Odor tests

It is emphasized that once a spill has occurred, qualitative analysis is useless without a source sample for comparison. That is, a representative OIL sample must be collected from the source, such as:

- 1 The ship - each compartment, bilge and ballast

2 Offshore platform

- 3 Terminal - each tank
- 4 Refinery - various process sources
- 5 Storm sewer - suspected sources

It may also be desirable to collect benthic, phytoplankton and zooplankton samples. However, this should only be done if BEFORE and AFTER samples can be obtained and only if a qualified staff of marine biologists are available for collection, preservation and analysis.

III SAMPLE COLLECTION

A Many precautions must be observed when handling oil samples for analysis since the character of the sample may be affected by a number of common conditions including:

- 1 Composition of the container — glass bottles should always be used since plastic containers, with the exception of teflon, have been found under certain conditions to absorb organic materials from the sample. In some cases, the reverse is also true in that compounds have been dissolved from the plastic containers into the sample itself. This problem also applies to the bottle cap liners; therefore, the portion of the cap that comes in contact with the sample should be made of

glass, teflon, or lined with aluminum foil.

- 2 Cleanliness of the container — previously unused glass bottles are preferred. If this is impossible, bottles should be either acid cleaned or washed with a strong detergent and thoroughly rinsed and dried.
- 3 Time lapse between sampling and analysis — since the chemical characteristics of most oils, especially the lighter fuel oils, change with time, the time lapse between sampling and analysis should be kept to a minimum. If analysis cannot be completed within 24 hours, samples can be preserved, depending upon the volatility of the oil, by removal of air and exclusion of light. With heavier type oils, such as No. 4 and residual oils, carbon dioxide may be used to displace the air. If dry ice is available, (approximately 0.5 cu. in.) it may be added to the sample. As soon as the effervescing has stopped, the jar should be sealed. When carbon dioxide or another inert gas is not available, or in those instances where volatile components are present (No. 2 or lighter), the sample can be preserved by carefully filling the bottle to the top with water to displace the air. All samples should be kept under refrigeration until analyses are completed.
- 4 Collection of adequate volume of sample — it is desirable to obtain as much of a sample of the oil as possible. It is suggested

that 20 mls be considered as the minimum volume of oil needed to perform a series of "identification analyses" on light oils — No. 2 and below. For heavier oils a minimum volume of 50 mls is required.

B Oil Sampling Techniques

Sampling of oil presents many difficulties not immediately obvious. An oil slick may vary in thickness from several inches down to a monomolecular layer measured in microns (10^{-4} cm.). The quantity of sample required is therefore important since such will determine the area of sweep. For example, 5,000 gallons of oil, if assumed to be evenly distributed over one square mile of water, will equate to an oil thickness of 0.0071 mm. If 200 ml of sample is found necessary, then all the oil must be recovered from 28 square meters of open water. If sampling recovery is 50 percent rather than 100 percent, the sweep area must be doubled. Table II below describes theoretical thickness and area, assuming an even distribution of oil for various magnitude oil spills.

TABLE II
OIL DISTRIBUTION ON A WATER SURFACE

<u>Spill Area</u> <u>Gal/Sq. Mile</u>	<u>Spill Area</u> <u>ml/Sq. Meter</u>	<u>Area (Sq. Meters)</u> <u>Req'd. to Obtain</u> <u>200 ml/sample</u>	<u>Oil</u> <u>Thickness (mm)</u>
1,000,000	1430	0.14	1.43
100,000	143	1.4	0.143
10,000	14.30	14	0.0143
5,000	7.15	28	0.0071
1,000	1.43	140	0.00143 = 1.43 μ
100	0.143	1400	0.000143 = 0.143 μ

C The ideal oil sampling device should contain the following characteristics:

- 1 Be simple to operate.
- 2 Function under diverse conditions.
- 3 Have a few moving parts and not require electrical power.
- 4 Be inexpensive.
- 5 Collect oil rapidly.
- 6 Not require chemical treatment of sample.

D Current Sampling Procedures

1 Manual Separation

Manual separation is the oldest

oil sampling procedure. The method involves collection of oil-water mixture in a container followed by manual separation of the oil and water phases. Collection and separation is continued until about 1 pint of oil has been collected. The procedure is quantitatively inaccurate because of the crude nature of both the collection and separation steps.

a Collection devices have included:

- 1 Simple pail
- 2 Pail fitted with a bottom tap
- 3 Sliding plexiglass cylinder whose fall is controlled by a trigger

- 4 Dustpan with a stopcock fitted to the handle

b Separation procedure devices have included:

- 1 Manual decantation
- 2 Separatory funnel
- 3 Glass filter funnel fitted with a two-way stopcock

2 Adsorbent Materials

Many materials strongly adsorb oil and other hydrocarbons. Such materials include teflon shavings, straw, polypropylene fiber, rope, glass fiber, paper, and polyurethane foam.

Qualitative sampling requires contact of the sorbent with the oil followed by chemical (desorption) or physical (wringing or compression) recovery of the sorbed hydrocarbon. Quantitative sampling requires contact of the sorbent with a known area of liquid surface; this application has been impeded by variable and uncertain adsorption efficiency.

a French scientists have studied two applications of textured filter paper.

- 1 Free floating disks
- 2 Lined cylindrical containers

At film densities of 650 to 2200 mg/sqm (2.6 ml/sqm at a density of 0.85) both methods sample quantitatively to $\pm 25\%$ with a single sample.

b Polyurethane foam

Adsorption by polyurethane foam appears to be a promising procedure. In practice a 1/4" x 1' sheet is simply dragged across the surface until apparent saturation is reached. The sheet is then passed through a wringer to recover the adsorbed oil.

When tested with South Louisiana crude oil this procedure recovered a sample containing less than 0.1 percent water. Infrared spectrographic analysis revealed no chemical differences between the original oil and the sample recovered.

IV DOCUMENTATION OF EVIDENCE AND SAMPLES

A Procedures for documentation of evidence and samples are specified by the National Oil and Hazardous Materials Pollution Contingency Plan and its regional derivatives. Collectively these plans guide the coordinated reaction of Federal, State, and local government and private agencies to uncontrolled discharges of hazardous materials. Documentation procedures include collection of samples from both the water course and suspected sources and preparation of a pollution incident report (Form FWPCA-209). These procedures have been

established to document the actual facts of an incident and to protect the interests of all parties.

- B After having been collected as outlined above each sample should be properly labeled using the chain of custody record, Form FWPCA-208 (See Figure 1). The record should contain the following information:

1 Sample collection data

This includes name and address of the agency submitting the sample number, data and time at which the sample was taken. A clear description of the source of the sample and the signatures of the sample collector and one or more witnesses. FAILURE TO OBTAIN THE SIGNATURES OF WITNESSES MAY RENDER THE SAMPLE LEGALLY INDEFENSIBLE. Witnesses should understand that by their signature they are certifying all information contained on the custody record, e.g., the date and time the sample was taken and description of its source.

2 Shipment certification

This information includes date and time the sample was submitted for shipment, the name of individual from whom it was received, the date and time it was dispatched, and the method of shipment, and the name and address of the consignee. All shipment information should be certified by an authorized representative of the common carrier or a postal official.

3 Certification of sample receipt

The individual receiving the sample should certify by signature the date and time of receipt, the name of the individual from whom the sample was received and the proposed disposition. If the sample is to be shipped to more than one laboratory, duplicate custody records bearing the same sample number should be completed.

- C In accordance with procedures identified in the Regional Contingency Plan the on-scene commander should prepare four copies of the pollution incident report, Form FWPCA-209 (See Figure 2). Copies of the report and additional documents and attachments should be distributed as follows:

- 1 The original and one copy to the Chairman of the Appropriate Regional Operations Team.
- 2 One copy to the Joint Operations Team.
- 3 One copy to the Headquarters of the agency supplying the on-scene commander.

Three areas of the pollution incident report are especially crucial: Section III Pollution Data, Section IV Pollution Sample, and the first

endorsement. As much data, facts, observation and information as possible should be included. All statements from persons directly concerned with the incident should be signed and witnessed. Although the on-scene commander may include other statements and comments, such information may not be entered as evidence.

V SUMMARY

A full scale oil sampling program is designed to collect samples, the analysis of which will be presented as legal evidence in a court of law. Qualitative and/or quantitative analysis will be performed on these samples which may include water, mud, fish and shellfish. What exactly is sampled depends on several parameters from the location of the spill to the analysis equipment available.

Sampling itself is more of an art than a science. Most methods are based upon manual collection in a container or adsorption and subsequent recovery. There is presently no recognized standard procedure.

Documentation of samples and evidence is required to adequately protect the interest of all parties to an incident. The conditions of collection, shipment and receipt of samples should be documented with utmost care to preclude later questions of validity.

References:

- 1 "Oil Sampling Techniques", Edison Water Quality Laboratory, Edison, New Jersey (December 1969).
- 2 "Oil Tagging System Study", Melpar (May 1970).
- 3 Proceedings, Joint Conference on Prevention and Control of Oil Spills, API/FWPCA (December 1969).

Outline prepared by J. S. Dorrlar, Acting Chief, Oil Research and Development Section, Edison Water Quality Laboratory, Edison, New Jersey 08817, January 1971.

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION		CHAIN OF CUSTODY RECORD	
NAME OF UNIT AND ADDRESS			
SAMPLE NO.	TIME TAKEN (Hours)	DATE TAKEN	
SOURCE OF SAMPLE			
NAME OF PERSON TAKING SAMPLE (First, Initial, Last Name)			
WITNESS(ES) TO TAKING SAMPLE (First, Initial, Last Name)			

FWPCA 206 (7-68)

RECEIPT OF SAMPLE	I hereby certify that I received this sample and disposed of it as noted below.		
	RECEIVED FROM	DATE RECEIVED	TIME RECEIVED
DISPATCH OF SAMPLE	DISPOSITION OF SAMPLE		SIGNATURE
	I hereby certify that I obtained this sample and dispatched it as shown below.		
	DATE OBTAINED	TIME OBTAINED	SOURCE
	DATE DISPATCHED	TIME DISPATCHED	METHOD OF SHIPMENT
	SENT TO		SIGNATURE

Figure 1

U.S. DEPARTMENT OF THE INTERIOR FEDERAL WATER POLLUTION CONTROL ADMINISTRATION POLLUTION INCIDENT REPORT		1. REPORTING UNIT		2. DATE OF REPORT		3. CASE NO.	
SECTION I - VESSEL DATA				7. HOME PORT			
8. NAME OF VESSEL		9. OFFICIAL NUMBER		10. COUNTRY OF REGISTRY			
10. INTERNATIONAL CALL		11. TYPE OF VESSEL (BY MAR. CODE, ETC.)		12. TYPE OF POLLUTION		13. OTHER IDENTIFYING INFORMATION (if available)	
14. OWNER'S OF VESSEL - name & address		15. LOCAL AGENT'S name & address		16. MASTER (name, address & license number)		17. CHIEF ENGINEER (name, address, & license no.)	
SECTION II - SHORE FACILITY DATA				18. TYPE OF REFUSE			
19. NAME AND ADDRESS OF COMPANY OR INDIVIDUAL				20. TYPE OF FACILITY			
21. OTHER IDENTIFYING INFORMATION							
SECTION III - POLLUTION DATA				22. TYPE & AMOUNT OF POLLUTANT			
23. PERSON REPORTING POLLUTION (name and address if available)		24. WITNESS name & address if available		25. PLACE OF POLLUTION (local name or geographic coordinates)		26. TYPE & AMOUNT OF POLLUTANT	
27. SIGNED STATEMENT ATTACHED		28. SIGNED STATEMENT ATTACHED		29. DATE		30. PHOTOGRAPH ATTACHED	
31. CASE OF POLLUTION (reason, report, etc.)		32. TYPE OF LICENSE OR CERTIFICATE HELD BY PERSON REPORTING		33. EMERGENCY MEASURES TAKEN TO REDUCE FIRE HAZARD		34. YES ☐ NO ☐	
35. NAME		36. NAME		37. LICENSE NUMBER (if applicable)		38. SIGNED STATEMENT ATTACHED	
39. YES ☐ NO ☐		40. YES ☐ NO ☐		41. YES ☐ NO ☐		42. YES ☐ NO ☐	
SECTION IV - POLLUTION SAMPLES				43. WITNESS			
44. SOURCE OF SAMPLE		45. DATE TAKEN		46. SAMPLE NO.		47. NAME OF PERSON TAKING SAMPLE	
48. YES ☐ NO ☐		49. YES ☐ NO ☐		50. YES ☐ NO ☐		51. YES ☐ NO ☐	
52. OPERATING PERSONNEL INVOLVED		53. NAME		54. DATE		55. YES ☐ NO ☐	

FUPCA 209 (7-48)

Figure 2

Oil Sampling Program

SECTION IV (Continued)

31. REMARKS (Give full description of incident, including attitudes of personnel and composition received. If necessary, continue on blank pages and attach.)

32. INVESTIGATING OFFICER (Name and title)		33. SIGNATURE OF INVESTIGATING OFFICER		33A. DATE SIGNED	
34. FROM		35. TO		36. FROM	
37. DATE		38. SIGNATURE		39. DATE	
39. SIGNATURE		40. SIGNATURE		41. DATE	

WPC-200 (7-48) (Reverse)

Figure 3

ANALYSIS OF OIL SAMPLES

I INTRODUCTION

A Oils and oil-water samples are analyzed to identify the type of spilled petroleum product or to establish similarity between samples collected from the environment and from suspected sources. Common origin is probable if samples agree in their key characteristics.

B Analysis is complicated by effects of environmental influences and lack of procedure adapted to oil-water mixtures. Petroleum analysis is based upon procedures developed with petroleum products.

C Analysis of environmental samples involves preliminary clean-up followed by standard analytical procedures. The complete analytical sequence shown in Figure 1 involves three levels of activity.

- 1 Preliminary clean-up intended to separate the oil from the water and produce an organic phase amenable to analysis.
- 2 Identification of spilled material as a specific type of petroleum product; e.g., gasoline, jet fuel, crude oil, etc. Identification is accomplished by analysis according to standard procedure and comparison of results with prescribed characteristics of typical petroleum products. Characteristics of a few such petroleum products are specified in Table 1.
- 3 Further analysis to more clearly define the relationship between the environmental sample and reference samples collected from suspected sources. Results of the analyses are used to evaluate similarity.

D Both the apparent and suspected nature of the sample will influence the actual laboratory procedure. The analyst himself will normally select the procedures necessary to accomplish identification or comparison. The required level of analysis (e.g., identification or identification/comparison) depends on the nature of the problem.

II CLEAN-UP

Sample clean-up is commonly accomplished by one of three basic methods:

A Simple Phase Separation is generally applicable to distillate fuel oils (Fuel oil nos. 1, 2, and 4, kerosine, gasoline, etc.), and consists of withdrawing the heavier aqueous phase from the lighter organic phase in a separatory funnel. The organic phase is then dried by passage through anhydrous CaCl_2 . The dissolved petroleum products may be "salted out" of the aqueous phase by the addition of Na_2SO_4 to the water.

B Drying with Centrifugation

When the petroleum product, as is the case with some crude oils and residual fuel oils, is emulsified with water and/or solid matter, it is sometimes possible to break the emulsion by removal of the water from the matrix with anhydrous calcium chloride, and then centrifuging the sample in a chemical centrifuge to isolate the oil phase as the centrifugate.

- C Phase Separation with Solvent Addition is accomplished by adding a solvent, such as chloroform to the oil-water mixture. It is sometimes possible to obtain a clean phase separation by solvent addition and to proceed as in A to separate the organic phase from the aqueous. The organic phase, after drying with calcium chloride, is heated to evaporate the solvent.

III IDENTIFICATION

- A When clean-up has been completed, the separated and dried organic phase, is subjected to analysis. Identification is normally accomplished by comparison of sample characteristics to those of typical petroleum products. Characteristics of a few typical products are specified in Table 1.

- B The analyses indicated in Figure 1 should be considered alternatives which the analyst may select to accomplish identification. Only a few analyses may be required in some cases, whereas in other cases the complete analytical scheme may be necessary. It is the responsibility of the analyst to select the combination which will accomplish the most certain identification in the time available.

C ANALYTICAL PARAMETERS

- 1 Solubility in Organic Solvents - Used to differentiate greases and asphalts from other petroleum products, and to distinguish between crude oils and residual fuel oils from different locations. Table 2 gives solubility characteristics for several typical petroleum products.
- 2 Specific or API Gravity - The gravity or density is a distinguishing characteristic of oils. However, as the loss of volatiles, which occurs in the early stages

of environmental exposure with volatile distillate fuels and crude oils, results in an increase of this parameter, it is of limited value.

- 3 Infrared Spectroscopy - Indicates the relative content of aromatic or carbon-ring-type compounds. May also indicate presence of additives such as silicones. Generally employed to characterize materials less volatile than #2 fuel oil, such as #4 and residual fuels.
- 4 Average Molecular Weight - Used to identify low and high boiling products. Not commonly employed with other than pure hydrocarbons.
- 5 Distillation Range - Defined as the temperature difference between high and low boiling compounds in an oil observed during distillation. Actual procedures are specified by ASTM D 86-56, ASTM D 850, and ASTM D 216. Reported as the actual temperatures at which distillation begins and ends: (1) I.B.P., initial boiling point, and; (2) E.P., ending boiling point. The boiling range relates to volatility. Although potentially valuable, IBP is useless if the oil has been subjected to weathering before collection due to volatilization of lower boiling components. Typical distillation ranges are presented in Table 1.
- 6 Viscosity - A measure of the resistance to flow. May be expressed as (a) Saybolt second units (SSU), the time required for a standard volume of oil to pass through a standard orifice, as specified by

ASTM D 445-53T and ASTM D 446-53; (b) kinematic viscosity at 100°F or 212°F in centistokes (ASTM D 445-65) or in Saybolt Furol units at 122°F. ASTM 2161-63T gives the relationships between the different viscosity units.

- 7 Distillation - As a loss of volatile components (if present) occurs on environmental exposure resulting in an increase of the remaining components, these may be put on the same basis (normalized) by distilling all samples to a similar degree. This is accomplished in our laboratory by distillation in a simple distillation apparatus to obtain a distillate boiling point of 275°C at 40 mm Hg pressure. The distillate is analyzed by gas chromatography and the residue for vanadium, nickel, sulfur, and nitrogen content and infrared analysis. Column chromatography may be incorporated in the analysis.
- 8 Vanadium is analyzed according to ASTM D 1548-63.
- 9 Nickel is analyzed either in the final solution from the vanadium procedure by atomic absorption (AAS) or by dissolving 5g oil in 100 ml of xylene for determination by AAS.
- 10 Sulfur is analyzed by the procedure described in ASTM D 1552-64, using the Leco induction furnace, or by ASTM D 129-64, utilizing an oxygen combustion bomb. In domestic fuel oils (1967), sulfur values ranged from 0.001 to 0.45% for #1 fuel oil; 0.02 to 1.6% for #2 fuel oil; 0.2 to 3% for #4 fuel oil; and 0.4 to 4.25% for #6 fuel oils.
- 11 Nitrogen is determined by the Kjeldahl method.

IV SUMMARY

Oil analysis involves three levels of laboratory activity: sample preparation and clean-up; basic identification; and final comparison. Identification as a petroleum product is accomplished by comparison of sample characteristics to prescribed properties of typical products. Further analysis may be performed to more firmly establish the similarity between environmental samples and reference samples collected from potential sources. At all stages of analysis the judgment of the analyst is crucial. Typical analyses include observation of solubility in organic solvents, infrared spectroscopy, API Gravity, distillation range, gas chromatography, specific metal determinations, viscosity measurement, and sulfur determination.

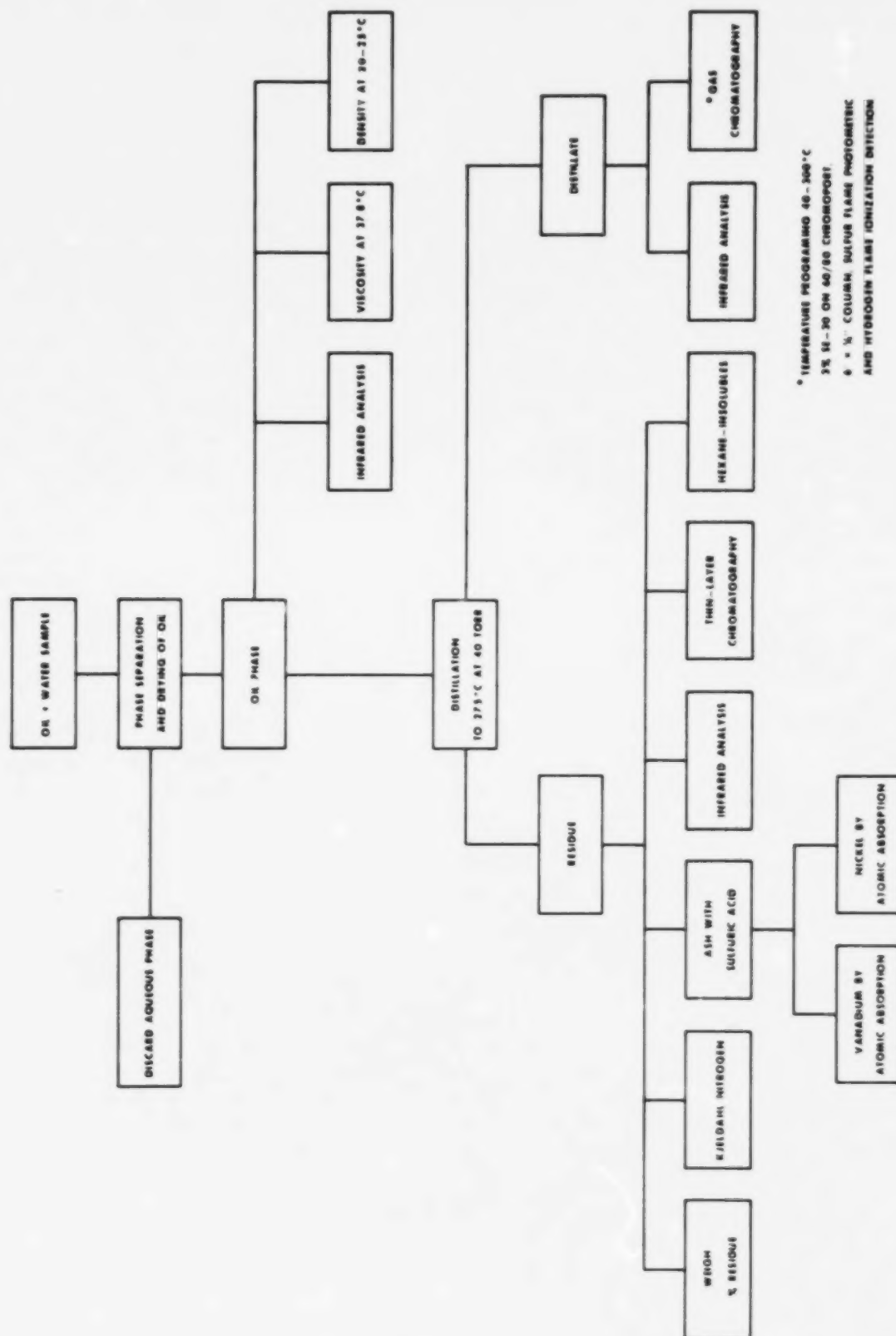
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Kahn, L., Unpublished data

This outline was prepared by L. Kahn, Chief Chemist, Laboratory Branch, Environmental Protection Agency, Edison Water Quality Laboratory, Edison, N.J. 08817, January 1971

ANALYTICAL SCHEME FOR CRUDE OILS



* TEMPERATURE PROGRAMMED 40-300°C
 3% SE-30 ON 60/80 CROMOPORT
 6' x 1/8" COLUMN, SULFUR FLAME PHOTOMETRIC
 AND HYDROGEN FLAME IONIZATION DETECTION

TABLE 1

CHARACTERISTICS OF STANDARD PETROLEUM PRODUCTS

PRODUCT	API GRAVITY (API UNITS)	KINEMATIC VISCOSITY (centistokes)	DISTILLATION RANGE (I.B.P. - E.P.)	COMMENT
High Gravity Naphtha	45 - 75		95° - 206° F	Sulfur 0.02%
Low Gravity Naphtha	30 - 53		160° - 410° F	
Gasoline	58 - 62		96° - 408° F	Contains lead, halogens
Jet Fuel	40 - 55		100° - 500° F	
Kerosine	40 - 46		355° - 575° F	Narrow API Gravity range
Fuel oil #1	> 35	1.4 - 2.2		
Fuel oil #2	> 26	< 4.3	370° - 675° F (90%)	Sulfur exceeds 0.5%
Fuel oil #4	9 - 36	5.8 - 26.4	420° - 683° F	
Crude Oil	13.5 - 33.5	2.3 - 10.5	40° - >850° F	Wide dist. range
Fuel Oil #6	-2 - 18	> 100	> 700° F	

TABLE 2
SOLUBILITY OF PETROLEUM PRODUCTS IN ORGANIC SOLVENTS

PRODUCT	SOLVENT	
	HEXANE	CHLOROFORM
LIGHT NAPHTHA	VS	VS
HEAVY NAPHTHA	VS	VS
GASOLINE	VS	VS
JET FUEL	VS	VS
KEROSINE	VS	VS
CUTTING OIL	S	S
MOTOR OIL	S	S
PARAFFIN WAX	S	S
WHITE PETROLEUM JELLY	PS	PS
GREASE	I	S
RESIDUAL FUEL OIL	PS	S
ASPHALT	I	S
VS = very soluble S = soluble PS = partly soluble I = insoluble		

PREVENTION AND CONTROL - TREATMENT

Tanker Operation

TANKER OPERATIONS

I INTRODUCTION

Various government and oil industry sources estimate that anywhere from 33,000 barrels of oil per day, up to ten million tons of oil per year foul the world's oceans and seas. This may be a conservative estimate.

II SOURCES OF OIL DISCHARGED INTO SEA FROM TANKER OPERATIONS

- A. Bilge Oil: Is that oil which collects in the ship's bottom through seepage or leakage.
- B. Slop Oil: Is that oil/water emulsion which is normally collected in an aft center tank as the residue of tank cleaning operations.
- C. Overflows: An overflow of oil usually occurs during the loading or discharge of cargo and the transfer of cargo from one tank to another. This is usually caused by carelessness or inattention.
- D. Ballast Water: This is normally sea water taken into empty cargo tanks to give the vessel stability. The "empty" cargo tanks usually have a residue of oil in them.
- E. Collision: Whenever a loaded tanker vessel is involved in a collision the results is usually a major discharge of oil into the surrounding waters.

III TANK CLEANING OPERATIONS

- A. Surface Area: The inner surface of a cargo tank, if inspected closely, would be found to be rough, uneven and pockmarked with thousands of minute pore openings. The total surface area of the interior of the cargo tanks of a T-2 tanker is approximately eight and one half acres.
- B. Clingage: When a beer glass is filled and emptied a certain amount of the liquid adheres to the side of the container. This is the liquid required to "wet" the surface of the container. It will vary in amount as a function of its viscosity, temperature, volatility and the roughness and configuration of the container.

In the same way, a certain quantity of oil under fixed conditions is required to wet the surface of the tanks of a tanker. Under average conditions based on long experience, it has been found that this quantity varies from 0.20% to 0.40% of the cargo. A median figure might be 0.30%. This means that if 250,000 barrels of average oil cargo were loaded into a tanker and the tanker immediately pumped out, only 99.7% of the oil would be recovered in the shore tanks and 0.30% or 750 barrels would remain in the ship. The oil remaining in the ship

would be found to be adhering to the tank surfaces with a very small portion laying in shallow puddles at the suction "bell mouths" in the tank and cargo piping.

- C. **Butterworth System:** An operation of great significance in connection with the waste oil resulting from tanker operation is the system used for cleaning or washing down the tanks. Until the early 1930's, the cleaning of tankers was accomplished by long periods of steaming followed by hand washing with streams from fire hoses. There was then developed a system for machine washing of the tanks consisting of opposed revolving nozzles connected to a hose lowered to various levels in the tank to be washed. These nozzles revolve around both a vertical and horizontal axis by the action of a water turbine driven by the washing water at a pressure of about 160 pounds per square inch and a temperature of 170 to 180°F. This is known as the Butterworth System.

IV LOAD ON TOP PROCEDURES

- A. **Background:** Shell introduced the 'load-on-top' system in 1962. Other major oil companies soon followed, and today, encouraged by the oil industry, about 75 per cent of the world's crude oil tankers practice the technique. Refineries of the major oil companies accepted 'load-on-top' residue after an experimental period in which they proved to themselves that the residue can be processed through the refinery units — if it is less than 1 per cent of the total crude cargo, and

if the water content of the residue is less than 0.15 per cent of the total cargo. The main problem facing the refinery operator is the removal of salt from the small amount of sea water discharged with the residue. The problem of the tanker operator, then, is to remove as much water as possible from beneath the oil—without discharging the oily waste itself.

- B. **Principals of System:** What are the principles of the Load-On-Top system? This is best described by Kluss: "In the 'load-on-top' system, tanks are washed in this way during the ballast passage. The tank washing residues are accumulated in one tank. Most of the clean water in this tank is then carefully drawn off the bottom of the tank and discharged overboard, discharge being halted whenever oil traces appear in the water stream. The tank is allowed to settle, the oil wastes in the tank separate and float to the surface, and additional water is repeatedly withdrawn carefully from the bottom and discharged as before from beneath the floating layer of oil. Heat may be applied to hasten the separation of oil and water. Some companies occasionally add a demulsifier as well. When all possible water has been withdrawn, the next cargo is loaded on top of the remaining residues in this tank. Usually, this one compartment is segregated from the remainder of the cargo during discharge. Then the segregated material can be directed, as the specific situation dictates, to the fuels processing side of the refinery, to the refinery slop system for ultimate recovery, or mixed with the rest of the cargo being discharged.

C. Pitching Ship: In a rolling pitching vessel, this is no small task. It is estimated that the oil content of the water discharged into the vessel's wake from the 'load-on-top' tank is in the region of 200 ppm, slowly increasing to 400 ppm and finally rising momentarily to 5000 ppm at the shut-off point. A tanker decanting this residue will not pollute the sea. Even the momentary maximum of 5000 ppm is only half of one per cent. The turbulence in the moving ship's wake would immediately dilute any oil to a tiny fraction of its original concentration. If a vessel experiences rough weather on its way to the loading port and the water in the 'load-on-top' is therefore not reduced to an acceptable level, fresh crude oil can still be loaded on top. But at the discharge terminal the mixture at the bottom of the tank must then be retained on board to be put through another 'load-on-top' cycle.

D. PPM of Oil Discharged - "Eye-ball Method": "Load-On-Top" is a questionable first step in the prevention of pollution of the sea by oil. There are too many questions left unanswered. Members of the oil-shipping industry admit that, at present, the best method of measuring the PPM of oil in an oily water discharge is by the "eyeball" method. This means that a member of the ship's crew must constantly watch the overboard discharge until black oil is seen with the naked eye. The crew member then signals to the pump man who in turn starts closing the discharge line. This may take from fifteen to thirty seconds. In the mean-

time, a significant amount of oil is lost overboard. In the "Load-On-Top" paper, the author admits that at times, the discharge of oily waste into the sea reaches a height of 5,000 PPM.

E. Emulsions: The basic problem of the "Load-On-Top" system is the question, "how much oil is contained in the water being decanted into the sea?"

Emulsions take either one of two forms—an oil in water emulsion or a water in oil emulsion. The latter, of which the famous "chocolate mousse" is formed, is much more difficult to break than the former. The oil industry as a whole, has spent literally millions of dollars trying to separate oil from their wastewater discharge. This is still a major problem in the industry today. If the sophisticated oil/water separators of the major refineries cannot successfully remove all of the oil from an effluent discharge, how can we believe that a simple type gravity separator on board a rolling ship can effectively accomplish this?

V TANKER TERMS

A. Gross Tonnage: One hundred cubic feet of permanently enclosed space is equal to one gross ton—it has nothing whatever to do with weight. This is usually the registered tonnage although it may vary somewhat according to the classifying authority or nationality.

B. Net Tonnage: This is the earning capacity of a ship. The gross tonnage after deduction of certain spaces, such as engine

and boiler rooms, crew accommodation, stores, equipment, etc. Port and harbor dues are paid on Net Tonnage.

- C. Displacement Tonnage: This is the actual weight in tons, varying according to whether a vessel is in a light or loaded condition. Warships are always spoken of by this form of measurement.
- D. Deadweight Tonnage: The actual weight in tons of cargo, stores, etc. required to bring the vessel down to her load line, from the light condition. Cargo deadweight is, as the name implies, the actual weight in tons of the cargo when loaded, as distinct from stores, ballast, etc.
- E. Innage: That space occupied in a product container.
- F. Outage: Space left in a product container to allow for expansion during temperature changes it may undergo during shipment and use.
- G. Ullage: That amount which a tank or vessel lacks of being full.

VI SINGLE POINT MOORING SYSTEMS

The tankers in the world fleet are growing bigger each year while the ports serving these supertankers are still in the World War T-2 class. The industry, therefore, advocates the Single Point Mooring System.

- A. Conventional Mooring System: The conventional mooring system uses fixed mooring buoys plus the fore and aft anchors of the vessel to be moored. The connecting hose to the underwater

pipeline is connected to a small floating buoy, which is retrieved when the ship is in a fixed position. The known objections to this system are: (1) the vessel cannot remain in this position in rough weather, and (2) when the weather turns bad, it takes too long for the ship to un-moor and lift anchors.

- B. "T"-Jetty Mooring System: Some of these jetties are as long as 6,000 feet. The "T" head at the end of the jetty can be constructed to berth as many as eight tankers simultaneously. One of the advantages of this type of installation is that four pipelines can service six to eight berths simultaneously. The disadvantages of this type of installation are:

- (1) Extremely expensive to construct.
- (2) Ships must stop off-loading during bad weather, and slip moorings.
- (3) Approach speed to the installation for large tankers can only be at 1/10 knots. The problem here is that tankers personnel cannot sense true speed during approach and if the vessel strikes the installation at speeds over 3/10 of a knot, a large amount of damage can be expected. A new experimental radar system is being tried to overcome this objection.

- C. Sea Island Mooring System: This system has the same advantages and disadvantages as the "T"-Jetty Mooring System. In the Sea Island System the oil can either be pumped ashore through underwater pipelines or the oil

can be stored on the island to be later trans-shipped to shore installations by smaller tankers and barges.

- D. Single Point Mooring System: While the Single Point Mooring is relatively new in the oil industry (1959), this system is gaining a widespread acceptance throughout the industry as a reasonable cost expense and an effective method to off-load or on-load a tanker. The Single Point Mooring System can handle tankers in much rougher weather than any of the aforementioned systems. One of the great advantages of this type of system is that the wind, high seas and tide forces straining against the ship is only 1/6 of the forces received at other mooring systems. This is due to the fact that the ship "weathervanes" around the Single Point Mooring System buoy, bow forward. At the present time, the industry considers the Single Point Mooring System as the next best thing to a harbor mooring. Shell Oil Company and IMODCO of California are the only two producers of SPM Systems at the present time. However, Standard Oil Company (N.J.) is in the process of patenting and constructing an SPM System utilizing a single anchor mooring which they believe will be superior to the present system. This SPM System, considered a third generation type, will have an underwater swivel joint. This buoy will have a rigid type conduit from the sea floor to a swivel connection approxi-

mately 70 feet below the water surface. When there are sufficient numbers of SPM buoys throughout the world, tankers will convert to bow loading manifolds. The cost of conversion to this type of loading will be approximately \$70,000 per tanker.

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This outline was prepared by H.J. Lamp'l, Oil Spills Coordinator, FWQA, Edison Water Quality Laboratory

CHEMICAL TREATMENT

Dispersants - Policy

EPA Tests

DISPERSANTS

I BACKGROUND HISTORY

As far back as the early 1930's water emulsifiable degreasers were used. These degreasers were developed to answer the need for effective methods of cleaning oily and greasy surfaces. They possessed the properties of dissolving or dispersing in the grease or oil, and making the resultant mixture dispersible in water so that it could be flushed away with water.

The early products were composed mostly of soaps and solvents. The demands of the petroleum shipping industry required products that could be used effectively aboard ship with seawater. This led to the use of materials other than soaps as emulsifying agents because soap breaks down in seawater. Sulfonated petroleum oils and later more sophisticated synthetic detergents made their appearance in these products.

These emulsifying degreasers were widely used aboard ship for engine room maintenance, as well as for the clean-out of petroleum cargo tanks prior to welding repairs and prior to upgrading of cargo.

Because of their effectiveness in clean-out of oil residues it was natural that they should be tried for treating oil spills. In some cases they were incorporated in oil slops prior to dumping overboard to minimize slick formation.

There are presently over 200 commercially available products which are claimed useful for dispersing oil from the surface of the water. These products have been referred to as "soaps", "detergents", "degreasers", "complexing agents", "emulsifiers", and finally "dispersants". This latter term describes best what this type of product is intended to accomplish — the dispersion of oil from the surface into and throughout the body of water — and therefore is the preferred terminology.

II COMPOSITION

The primary components of dispersants are surfactants, solvents and stabilizers.

A Surfactants or Surface Acting Agents (SAA)

This is the major active component in dispersants.

By their affinity for both oil and water, surfactants alter the interaction between oil and water so that the oil tends to spread and can be more easily dispersed into small globules — or what we commonly call an emulsion.

These agents are often defined according to their behavior in aqueous solutions. These solutions will usually wet surfaces readily, remove dirt, penetrate porous materials, disperse solid

particles, emulsify oil and grease and produce foam when shaken. These properties are interrelated; that is, no surface active agent possesses only one of them to the exclusion of the rest.

SAA can be divided into two broad classes depending on the character of their colloidal solutions in water. The first class, ionic, form ions in solution, and like the soaps are typical colloidal electrolytes. The second class, the non-ionic, do not ionize, but owe their solubility to the combined effect of a number of weak solubilizing groups such as ether linkages or hydroxy groups in the molecule. A more detailed discussion of SAS is covered in reference (1).

Commonly used SAA in oil spill dispersants include soaps, sulfonated organics, phosphated esters, carboxylic acid esters of polyhydroxy compounds, ethoxylated alkyl phenols and alcohols (APE, LAE), block polymers and alkanolamides.

B Solvents

Since many of the surface active agents applicable to oil spill dispersant compounding are viscous or solid materials, some form of solvent is often necessary in order to reduce viscosity for ease of handling. In addition, the solvent may act to dilute the compound for economic

reasons, to depress the freezing point for low temperature usage, to enable more rapid solubility in oil, and to achieve optimum concentration of surface active agent for performance reasons. The presence of a suitable solvent also serves to thin the oil to be dispersed, reducing viscosity and making it more easily emulsifiable. The solvent usually comprises the bulk of the dispersant product.

The three general classes of solvents used in oil spill dispersants are petroleum hydrocarbons, alcohols or other hydroxy compounds, and water.

1 Petroleum Hydrocarbons

Petroleum fractions with boiling points above 300°F are usually used, and these may produce finished dispersants with flash points as low as 110°F. The proportion of aromaticity is of concern, since this affects solubility and emulsification properties as well as toxicity. Wardley Smith, Warren Springs Lab, UK, in describing the Torrey Canyon incident, reported that the aromatic solvents used were 10 times as toxic to marine life as were the surface active agents. Some typical fractions of applicable petroleum solvents include mineral spirits, kerosene, #2 fuel oil, and heavy aromatic naphthas which contain significant quantities of higher alkylated benzenes.

2 Alcoholic or Hydroxy Group of Solvents

Includes alcohols, glycols and glycol ethers. These solvents also lower the viscosity as well as the freezing points of finished dispersants. In addition, they furnish a co-solvent effect, often needed to mutually dissolve the various ingredients in a dispersant for stability of the compound in storage. This group of solvents may be used in conjunction with petroleum hydrocarbons as well as with aqueous solvent systems. Some of the more frequently encountered chemicals in this group include ethyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, ethylene glycol mono methyl ether, ethylene glycol mono butyl ether, and diethylene glycol mono methyl ether. The more volatile members of the group are quite flammable.

3 Water

Least toxic, least hazardous and most economical of the solvents. It lacks solubility or miscibility with oils. Where water is used as the solvent, special problems exist in the choice of surface active agents and other additives in order to provide the necessary miscibility with oils. Glycols and alcohols are used to aid in miscibility as well as freezing point depression

when water is used.

C Additives - Stabilizers

Third major component in dispersants, they may be used to adjust pH, inhibit corrosion, increase hard water stability, fix the emulsion once it is formed, and adjust color and appearance.

III DISPERSANT USE

A General

Dispersants theoretically serve to increase the surface area of an oil slick and disperse oil globules throughout the larger volume of water thereby aiding in accelerated degradation of oils by microbiological means. The chemical dispersants do not themselves destroy oil. They vary considerably in toxicity, effectiveness and ability to stabilize the oil after extended periods of time. Technology for proper application of dispersants over large oil slicks with necessary mixing is currently lacking. Use appears far more critical in harbor and estuary areas and in proximity to shore. Particular care must be exercised where water supply might be affected. The desirability of employing dispersants in the open sea remains unresolved although their use here (the ocean) is potentially more promising pending additional field data. After widespread dispersant use during major incidents, reports led to the conclusion that dispersants or the dispersant-oil mixture caused more

damage to aquatic life than the oil alone. For beaches, they actually compounded the problem by adding to the amount of pollutants present, by causing the oil to penetrate more deeply into the sand, and by disturbing the sand's compactness, so as to increase beach erosion through tidal and wave action.

B Toxicity

Current information indicates that dispersants vary considerably in toxicity. The combination of oil and dispersant may increase the toxicity of either the oil, the dispersant chemical or both. The possibility of this "synergistic" action must be carefully examined before wholesale application of such a product is permitted. Dispersing of the oil, which has toxic components, may also compound the damage.

The toxicity of 40 dispersants, as reported by the Fisheries Laboratory, Burnham on Crouch, UK, is shown in Table I. It is important to point out that the dispersants used during the Torrey Canyon incident were mostly solvent based and highly toxic, killing marine organisms at concentrations of 10 mg/l. Chemicals available today are much less toxic.

C Application⁽²⁾

A common method of dispersant application is by the water eductor method. A controlled amount of dispersant is sucked into a water stream such as a fire hose. This water jet is an effective vehicle or carrier for the dispersant and provides good coverage in treating the slick.

This application procedure however, while compatible with a water base system, may be

incompatible with a petroleum base system. This is because a dispersion of the petroleum solvent-in-water is formed as soon as the surfactant system is educted into the water stream. As illustrated in Figure 1 this accounts for the milky white appearance of the water after such applications. In this state, as graphically shown in Figure 1, it is difficult for the surfactant to transfer from its thermodynamically stable location at the petroleum solvent-water interface to the oil spill-sea water interface. Therefore, for a petroleum base system, neat application of the chemical directly onto the oil slick is a more effective application method.

The prompt application of mixing energy after the dispersant (solvent or water base) has been applied is particularly important. In essence, small oil droplets must be produced while the immediate water environment is surfactant-rich.

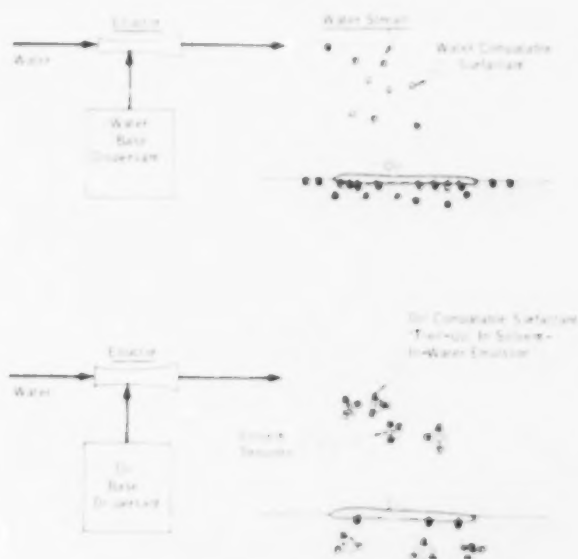


Figure 1

TABLE 1 (3)

Static Bioassays - TL50 48 Hours @ 15°C (ppm)

Solvent emulsifiers	<u>Pandalus</u> <u>montagu</u>	<u>Crangon</u> <u>crangon</u>	<u>Cardium</u> <u>edule</u>	<u>Agonus</u> <u>cataphractus</u>	<u>Flat Fish</u> <u>Pleuronectes</u> <u>limanda(L)</u>	<u>Asterias</u> <u>rubens</u>	<u>Garcinus</u> <u>maenas</u>	<u>Ostrea</u> <u>edulis</u>
	Pink Shrimp	Brown Shrimp	Cockle	Armed Bull Head	or Platessa(P) or Flessa(F)	Star Fish	Shore Crab	Oysters
Gamlen OSR	12.5	8.8	15.8				20.4	15-50
Polyc lens	9.5	15.7	70				23.2	
Six	12.1	114.5	12.7				> 300 (15)	100
BP 1002	5.8	5.8	81		10-33 (L)		10-25	50-100
Cleanosol	32	44	19.2				102	
Essolve	8.6	9.6	63				15-20	50-100
Gamlen D	11.5	9.6	34.8					
Gamlen CW	14.6		69.5					
Atlas 1901	87.2	120	48.5					
Slickgone 1	5.2	6.6	32.4				> 150	
Slickgone 2	4.5	3.5	30.5				35.0	
Shamash R1885	1-3.3	3.3-10					21.3	
Crow Solvent M		33-100						
DS 4545		~ 1000						
DS 4545 in Pink Paraffin		330-1000						
DS 4545 in IPA		3300-10000	330-1000					
DS 4545 in IBA		330-1000						
Aquacene		100-330	33-100					

*Tests lasted 5 days, not 48 hours.

Solvent emulsifiers (continued)	<u>Pandalus</u> <u>montagu</u>	<u>Crangon</u> <u>crangon</u>	<u>Cardium</u> <u>edule</u>	<u>Agonus</u> <u>cataphractus</u>	<u>Flat Fish</u> <u>Pleuronectes</u> <u>limanda(L)</u> or <u>platessa(P)</u> or <u>flesus(F)</u>	<u>Asterias</u> <u>rubens</u>	<u>Carcinus</u> <u>maenas</u>	<u>Ostrea</u> <u>edulis</u>
	Pink Shrimp	Brown Shrimp	Coekle	Armed Bull Head		Star Fish	Shore Crab	Oysters
Esso Solvent FG155		10-33						
Banner DG01		10-15						
Banner DG02		5-12						
Banner DG03		10-15						
Banner DG04		15-20						
Basol AD6		10-15						
Cuprinol 106		4-8						
Penetone X		20-30						
Polycrux A		100-200	33-100		33-100 (L)			
Graine OSR		500-750						
Corexit 7664		7500-10000	3300-10000		1000-3300 (L)			
Mobilsol		10-33						
Houghtosolve		10-33						
Raynap Sol B		3.3-10						
Foilzoll		330-1000	33-100					
BP 1100	>	3300	1000-3300	1000-3300				
Ridzlik		330-1000						
Dermol	148	156	148					
Corexit 9666	>	3300						
New Dispersol OS (Dispersol SD)		3300-10000		100-330				
New BP 1100 A	>	3300						
New BP 1100 B	>	3300						
Finasol ESK		100-330						
Finasol SC		33-100						
Hoe SC 1708		330-1000						
Snowdrift SC 98		330-1000						
Neptune Marine Cleaner		33-100						
Finasol OSR		3300						
BP 1100 A		3300-10000						
Sefoll		1000-3300						

D Cost-Effectiveness

1 Cost

The cost of dispersants ranges from \$2.00 - \$5.00 per gallon. Using manufacturers' recommended doses, which are usually 1 gallon of dispersant to 10 gallons of oil, the cost of chemicals for dispersing a relatively small 500 barrel spill would be about \$10,000.

Based on EPA's actual field experience, which has indicated that frequently the necessary dosage is 1 to 1 or 1 to 2, the cost might run as high as \$100,000 for this same size spill. Of course, the amount of chemical required is going to depend heavily on the type and age of oil to be treated, type of dispersant used, and the temperature of the water.

2 Effectiveness

Equally as important as toxicity, is the effectiveness of a dispersant.

Evaluation of the effectiveness of dispersants during accidental spill incidents is difficult. Lack of adequate methods for measuring the amount of oil on water and the rate of natural dispersion make precise evaluation impossible. Their effectiveness during the TORREY CANYON is still being debated. Subsequent incidents which are claimed to have demonstrated their effectiveness have been

at remote locations and without impartial, qualified observers. Application methods of dispersants and subsequent agitation, which are critical for effective performance, have not always been optimal.

As an initial step in trying to solve this problem EPA developed a standard test for measuring emulsion efficiency⁽⁴⁾. At the present time, four private labs are "testing the test" to determine its applicability using a variety of oils and dispersants. Figure 2, which shows the results of testing done at the Edison Water Quality Lab adequately demonstrates the degree of variability which will occur when using different dispersants on the same type of oil and when using the same dispersant on different types of oil.

E EPA Policy

The present policy regarding the use of dispersants is shown on the following pages.

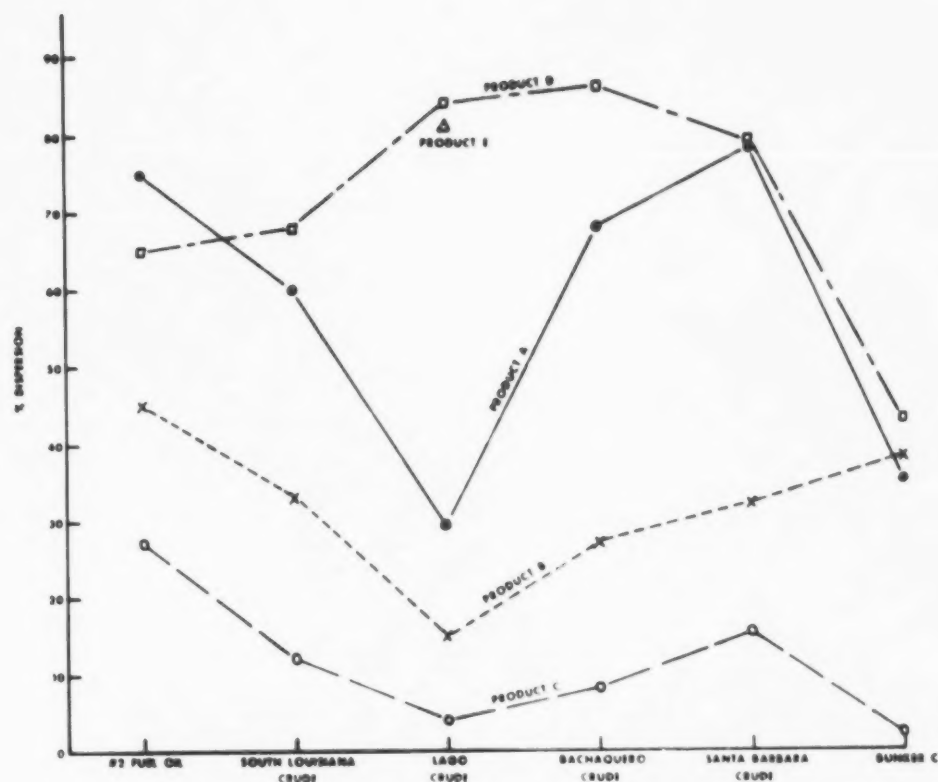


TABLE 2
APPARENT COMPOSITION OF TEST CHEMICALS

Product	Surfactant Ionic Nature ¹	Surfactant Basic Composition ²	Solvent ³
A	Nonionic	Ethylene oxide condensate of alkylphenol	Aromatic, aliphatic hydrocarbon, boiling point range similar to that of number 2 fuel oil
B	Nonionic	Ethylene oxide condensate of alkylphenol	Water, glycol
C	Nonionic	Polyhydric alcohol ester of fatty acid	Water, short chained alcohol
D	Nonionic	Alkanolamide	Water
E	Anionic	Alkyl aryl sulfonate	Aromatic, aliphatic hydrocarbon, boiling point range similar to that of number 2 fuel oil

¹ According to Weatherburn test.¹⁹

² By infrared spectral analysis of dried (105°C) residue; test was not definitive, but results consistent with stated, presumed composition.

³ By distillation and infrared spectral analysis.

Fig. 2: Oil Dispersant Effectiveness

ANNEX X(5)

2000 SCHEDULE OF DISPERSANTS AND OTHER CHEMICALS TO TREAT OIL SPILLS

2001 General

2001.1 This schedule shall apply to the navigable waters of the United States and adjoining shorelines, and the waters of the contiguous zone as defined in Article 24 of the Convention on the Territorial Sea and the Contiguous Zone.

2001.2 This schedule applies to the regulation of any chemical as hereinafter defined that is applied to an oil spill.

2001.3 This schedule advocates development and utilization of mechanical and other control methods that will result in removal of oil from the environment with subsequent proper disposal.

2001.4 Relationship of the Federal Water Quality Administration (FWQA) with other Federal agencies and State agencies in implementing this schedule: in those States with more stringent laws, regulations or written policies for regulation of chemical use, such State laws, regulations or written policies shall govern. This schedule will apply in those States that have not adopted such laws, regulations or written policies.

2002 Definitions Substances applied to an oil spill are defined as follows:

2002.1 Collecting agents - include chemicals or other agents that can gell, sorb, congeal, herd, entrap, fix, or make the oil mass more rigid or viscous in order to facilitate surface removal of oil.

2002.2 Sinking agents - are those chemical or other agents that can physically sink oil below the water surface.

2002.3 Dispersing agents - are those chemical agents or compounds which emulsify, disperse or solubilize oil into the water column or act to further the surface spreading of oil slicks in order to facilitate dispersal of the oil into the water column.

2003 Collecting Agents Collecting agents are considered to be generally acceptable providing that these materials do not in themselves or in combination with the oil increase the pollution hazard.

2004 Sinking Agents Sinking agents may be used only in marine waters exceeding 100 meters in depth where currents are not predominantly on-shore, and only if other control methods are judged by FWQA to be inadequate or not feasible.

2005 Authorities Controlling Use of Dispersants

2005.1 Regional response team activated: dispersants may be used in any place, at any time, and in quantities designated by the On-Scene Commander, when their use will

2005.1 - 1 in the judgment of the On-Scene Commander, prevent or substantially reduce hazard to human life or limb or substantial hazard of fire to property;

2005.1 - 2 in the judgment of FWQA, in consultation with appropriate State agencies, prevent or reduce substantial hazard to a major segment of the population(s) of vulnerable species of waterfowl; and

2005.1 - 3 in the judgment of FWQA, in consultation with appropriate State agencies, result in the least overall environmental damage, or interference with the designated uses.

2005.2 Regional response team not activated: provisions of Section 2005.1-1 shall apply. The use of dispersants in any other situation shall be subject to this schedule except in States where State laws, regulations, or written policies that govern the prohibition, use, quantity, or type of dispersant are in effect. In such States, the State laws, regulations or written policies shall be followed during the cleanup operation.

2006 Interim Restrictions on Use of Dispersants for Pollution Control Purposes Except as noted in 2005.1, dispersants shall not be used.

2006.1 on any distillate fuel oil;

2006.2 on any spill of oil less than 200 barrels in quantity;

2006.3 on any shoreline;

2006.4 in any waters less than 100 feet deep;

2006.5 in any waters containing major populations, or breeding or passage areas for species of fish or marine life which may be damaged

or rendered commercially less marketable by exposure to dispersant or dispersed oil;

2006.6 in any waters where winds and/or currents are of such velocity and direction that dispersed oil mixtures would likely, in the judgment of FWQA, be carried to shore areas within 24 hours; or

2006.7 in any waters where such use may affect surface water supplies.

2007 Dispersant Use Dispersants may be used in accordance with this schedule if other control methods are judged to be inadequate or infeasible, and if:

2007.1 information has been provided to FWQA, in sufficient time prior to its use for review by FWQA, on its toxicity, effectiveness and oxygen demand determined by the standard procedures published by FWQA. (Prior to publication by FWQA of standard procedures, no dispersant shall be applied, except as noted in Section 2005.1-1 in quantities exceeding 5 ppm in the upper 3 feet of the water column during any 24-hour period. This amount is equivalent to 5 gallons per acre per 24 hours.);

2007.2 applied during any 24-hour period in quantities not exceeding the 96 hour TL₅₀ of the most sensitive species tested as calculated in the top foot of the water column. The maximum volume of chemical permitted, in gallons per acre per 24 hours, shall be calculated by multiplying the 96 hour TL₅₀ value of the most sensitive species tested, in ppm, by 0.33; except that in no case, except as noted in Section 2005.1-1, will the daily application rate of chemical exceed 540 gallons per acre or one-fifth of the total volume spilled, whichever quantity is smaller.

2007.3 Dispersant containers are labeled with the following information:

2007.3 - 1 name, brand or trademark, if any, under which the chemical is sold;

2007.3 - 2 name and address of the manufacturer, importer or vendor;

2007.3 - 3 flash point;

2007.3 - 4 freezing or pour point;

2007.3 - 5 viscosity;

2007.3 - 6 recommend application procedure(s), concentration(s), and conditions for use as regards water salinity, water temperature, and types and ages of oils; and

2007.3 - 7 date of production and shelf life.

2007.4 Information to be supplied to FWQA on the:

2007.4 - 1 chemical name and percentage of each component;

2007.4 - 2 concentrations of potentially hazardous trace materials; including, but not necessarily being limited to lead, chromium, zinc, arsenic, mercury, nickel, copper or chlorinated hydrocarbons;

2007.4 - 3 description of analytical methods used in determining chemical characteristics outlined in 2007.4-1, 2 above;

2007.4 - 4 methods for analyzing the chemical in fresh and salt water are provided to FWQA, or reasons why such analytical methods cannot be provided;

2007.4 - 5 for purposes of research and development, FWQA may authorize use of dispersants in specified amounts and locations under controlled conditions irrespective of the provisions of this schedule.

REFERENCES

- 1 Poliakoff, Melvin, A., "Oil Dispersing Chemicals", 1969, Edison Water Quality Laboratory, FWPCA, Edison, New Jersey 08817.
- 2 Canevari, G. P., "General Dispersant Theory", Proceedings, Joint Conference on Prevention & Control of Oil Spills, API-FWPCA, 1969.
- 3 Portmann, J. E., "The Toxicity of 120 Substances to Marine Organisms", Fisheries Laboratory, Burnham on Crouch, Essex, United Kingdom, September 1970.
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Outline prepared by Richard T. Dewling,
Director, R&D, Edison Water Quality
Laboratory, December 1970.

PROPOSED EPA TESTS ON OIL DISPERSANT TOXICITY AND EFFECTIVENESS

I INTRODUCTION

Damage to the environment from oil spill clean-up operations by the indiscriminant use of chemical dispersants has led to the establishment of very restrictive policies regarding the use of these materials. These restrictions are set forth in the June 1970 National Oil and Hazardous Materials Pollution Contingency Plan which was developed pursuant to the provisions of the Water Quality Improvement Act of 1970. Among other constraints, it is the policy of this plan that oil dispersing chemicals, prior to their use, be tested for relative toxicity and effectiveness in accordance with standardized procedures to be established by the Federal Water Quality Administration. Data on the relative toxicity and effectiveness of these dispersing chemicals will provide the basis for the selection of those chemicals most effective and least toxic to aquatic life and for recommending or prohibiting their use.

In the fall of 1969, the Federal Water Quality Administration's National Marine Water Quality Laboratory at West Kingston, Rhode Island, provided preliminary methods for determining the relative toxicity of dispersants, while FWQA's Edison Water Quality Laboratory at Edison, New Jersey completed work on tentative procedures for evaluating dispersant effectiveness. Shortly thereafter, a joint government/industrial task force panel reviewed the proposed tests developed by these labor-

atories and recommended that an independent evaluation of the tests be conducted prior to official promulgation. Accordingly, an intensive program, sponsored by FWQA, is currently underway by four commercial laboratories to evaluate the reproducibility of the proposed tests and to recommend modifications, improvements and refinements in the testing procedures. This program is scheduled to be completed by June 1971.

II PROPOSED FWQA DISPERSANT TOXICITY TESTS

A General Description

These tests involve numerous bioassays on four aquatic organisms using the dispersant under investigation and mixtures of the dispersant with various oils. The test procedures require determinations of 96 hour (for fish) and 48 hour (for organisms other than fish) 50% survival values (IL_{50}) for both the raw dispersing chemical and dilutions of the dispersant mixed in a 1:10 ratio with each of two crude oils and two fuel oils. All test operations are carried out at 20°C for marine species and 25°C for fresh water species.

B Standardized Test Conditions

The bioassay methods stipulated in the tests are based on "Standard Methods for the Examination of Water and Wastewaters", 12th Edition, but they are modified to meet

the special problems arising in the use of fish and of test organisms other than fish in the bioassay of dispersants and mixtures of dispersants with different petroleum products. These modifications include special bioassay methods for organisms other than fish and the standardization of certain aspects of the bioassays outlined in "Standard Methods" such as test species, mixing and agitation, dilution water, aeration, dissolved oxygen concentrations, temperatures, pH and salinity.

The complete testing procedures are described in reference (4).

C Test Organisms

The four species designated for these tests are:

1 For Marine Water Determinations

- a Mummichog (Fundulus heteroclitus) Salt Water Fish
- b Oyster Larvae (Crassostrea virginica) - Soft Shell Invertebrate
- c Brine Shrimp (Artemia) - Hard Shell Invertebrate

2 For Fresh Water Determinations

- a Fathead Minnow (Pimephales promelas) - Fresh Water Fish

These four species were selected because they are widely distributed and, with the exception of the oyster

larvae, can be secured in most any portion of the country. The three test animals used in the marine water determinations represent a wide range of animal classes including: a free swimming fish; a mollusc (oyster) which is a bottom dwelling organism and is stationary at least part of its life; and an anthropod (shrimp) which represents the largest class of animal species. The animals selected for these tests also provide a wide range of indicators for relative toxicity. The fresh and marine water fish are somewhat tolerant animals, while the brine shrimp and oyster larvae are sensitive species highly susceptible to environmental insults.

D Test Oils

The oils used in these tests were selected on the basis of their availability and their composition, so as to reflect the varied range of oils likely to be encountered during spills. The selected oils are:

- 1 A refined product (No. 2 fuel oil) per ASTM Specification D-396-67.
- 2 A heavy residual fuel oil (No. 6 fuel oil) per ASTM Specification D-396-67.
- 3 A heavy, high asphaltic Venezuelan crude oil (Bachaquero) with the characteristics shown below.
- 4 A light, low residual crude (South Louisiana) with the characteristics shown below.

	<u>Bachaquero</u>	<u>South Louisiana</u>
API°	17	36.6
Viscosity, Universal 100°F	1500	41
Pour Point, °F	-5	15
% Weight Sulfur	2.2	0.20
% Weight Asphaltenes	7.0	0.3
Neutralization Number	2.7	0.4
% Volume Distilled at:		
300°F	6	18
400°F	17	43
700°F	35	71

E Discussion

The prime purpose of the FWQA Dispersant Toxicity Tests is to provide data which will indicate relative short term (acute) toxicity of dispersants and oil dispersant mixtures. These tests do not indicate the long term toxicity of these chemicals to aquatic organisms, safe levels for the aquatic biota or for humans, nor do they constitute an endorsement of any material by the FWQA.

III PROPOSED FWQA DISPERSANT EFFECTIVENESS TESTS

A General Description

These tests essentially incorporate the basic apparatus of the Navy Tank Test of Specification MIL-S-22864, Solvent-Emulsifier, Oil Slick with substantial procedural and equipment modifications to more closely simulate environmental conditions. The tests utilize a 24-inch diameter x 28-inch high cylindrical tank con-

taining 18-inches of standardized synthetic sea water with a system for recirculating the tank contents from the bottom of the tank to just below the surface of the water. This simulates the subsurface mixing of natural waters. In the test, 100 ml of oil is poured into a 7.5 inch diameter stainless steel ring which is positioned at the water's surface. The ring is used to contain the oil and facilitate contact between the oil and the dispersing chemical. The dispersant to be investigated is applied (in varying quantities) in a fine stream to the oil and a predetermined "contact time" is allowed for the chemical to contact the oil. The oil/dispersant mixture is then agitated by hosing with a pressurized stream of synthetic sea water under standard conditions until the water level in the tank reaches 18-inches. At the termination of hosing, the tank contents are allowed to recirculate throughout the sampling period. For determination of "initial dispersion" the samples are withdrawn 5 minutes after termination of hosing, which is the shortest time required for the

contents of the tank to stabilize; for determination of dispersant "stability", samples are withdrawn at stipulated intervals for periods of up to 6 hours after termination of hosing. Oil is extracted from the samples with an organic solvent and the quantity of oil is spectrophotometrically determined. Results of tests are expressed as percent of the original 100 ml of oil dispersed — that is, recovered from the underlying water.

In these tests, varying quantities of the dispersant under investigation are mixed with a constant quantity of oil (100 ml) in order to establish the minimum quantity of dispersant required for an "initial dispersion" of 25%, 50% and 75% of the total oil sample.

"Stability" determinations are made with that quantity of dispersant which causes a 50% "initial dispersion" of the oil. The "stability" tests measure the relative persistence of the dispersion for periods of up to 6 hours of mild agitation and basically follow the time course in the decay of the "initial dispersion".

It has been found that the time between addition of dispersing chemical and agitation (contact time) may have a profound influence on dispersant effectiveness, i.e. longer contact time improves the effectiveness of some dispersants and reduces that of others. For this reason, the contact time in this test is adjusted, to some extent, to the properties of the dispersing chemical used. This adjustment is made by determining initial dispers-

ion values of the chemical at widely differing contact times (zero and 10 minutes) and by performing all subsequent tests at that contact time giving greater dispersion.

Since eduction is frequently suggested by manufacturers as a method for applying dispersants, these tests include determinations of dispersant effectiveness when educted into the agitation hose stream as compared to effectiveness when applied undiluted to the oil followed by agitation.

More details of the Proposed FWQA Dispersant Effectiveness Tests are given in reference (5).

B Test Oils

The oils used in these tests are the same as those designated for the FWQA Dispersant Toxicity Tests.

C Discussion

The FWQA Dispersant Effectiveness Tests, which measure both initial dispersion and stability of dispersion and simulate typical environmental conditions, have been found by the Edison Water Quality Laboratory to produce results which correspond favorably with field performance. The tests show promise of providing meaningful measures of the effectiveness of chemicals in dispersing oil from the surface of water.

IV SUMMARY

Test procedures have been proposed by

the Federal Water Quality Administration for determining the relative toxicity and effectiveness of oil dispersing chemicals. The dispersant toxicity tests include bioassay determinations on four aquatic organisms using the dispersant under investigation and mixtures of the dispersant with two crude oils and two fuel oils. The dispersant effectiveness tests are basically modifications and refinements of the Navy specification for solvent emulsifiers. These tests measure the relative efficiency of the dispersant in varying concentrations with the designated oils.

It is expected that upon completion of the current evaluations of these proposed tests by the four commercial laboratories, meaningful standard procedures will be finalized which will be reproducible from day to day and from laboratory to laboratory. These tests should provide the necessary tools for the selection of relatively non-toxic, effective dispersing chemicals for oil cleanup operations.

REFERENCES

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- 3 "Standard Methods for the Examination of Water and Wastewaters", 12th Edition, American Public Health Association, New York, 1969.
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PHYSICAL METHODS OR TREATMENT

Sinking and Burning Agents

Sorbents

Booms

Skimmers

Beach Cleanup Methods

SINKING AGENTS

I DEFINITION - USE POLICY

Sinking agents are oil-attracting and water repelling sorbent materials designed to sink oil slicks out of sight rather than agglomerating oil on the water surface. The use of oil sinkants would seem advantageous in deeper waters outside heavy fishing zones, such as off the continental shelf and where adverse effects upon biological bottom life may be held at a minimum.⁽⁸⁾ Existing EPA policy on sinking agents restricts their use to waters exceeding 100 meters in depth.

Oily discharges into inland rivers and coastal waters do not remain floating forever since much of the oil will be naturally absorbed onto clay, silt and other particulate matter normally suspended in the water, thus causing eventual sinking of the oil. Sinking by natural means, for example, is believed to be one of the primary causes for the disappearance of oil slicks in the New York Harbor complex.

II TYPES

Various types of natural materials and commercial products are presently available which are claimed to be effective in sinking oil slicks.^(1,3) Typical agents include sand, brick dust, fly ash, china clay, volcanic ash, coal dust, cement, stucco, slaked lime, spent tannery lime, carbonized-siliconized-waxed sands, crushed stone, vermiculite, kaolin, fuller's earth, and calcium carbonate, including the "Oyma" type chalk used during the TORREY CANYON.

Sinking agents are believed most efficiently employed on thick, heavy and weathered oil

slicks in contrast to relatively light and fresh oils. These agents are granular or fine particulate solids with a specific gravity generally between 2.4 and 3.0. These agents must be evenly distributed over the surface of a slick and supplied with proper mixing, agitation and time interaction. The particle-coated and agglomerated mass eventually becomes heavier than water and sinks to the bottom.

III PERFORMANCE

The major problem in sinking oils is that the bonding of the agent with the oil must be nearly permanent. Experiments in both the laboratory and field show that many agents will release entrapped and sunken oils back to the water environment. Increasing the application rate two or three times over prescribed amounts has served to minimize this release.

Studies conducted by various investigators (4,5,6,7,9,10,12) indicated that:

- 1 Sulfurized oils may show greater sinking abilities than desulfurized oils because of higher potentials for hydrogen bonding.
- 2 When sands are used for sinking it may be expected that the oily mass will be stable under water when the sands are closely packed and the interstices are filled with oil giving an oil content around 40 per cent and a bulk density about 1.7. However, when the sands are loosely

packed, the mass will become internally mobile so that oil drops will separate and escape to the water until equilibrium is re-established.

- 3 With carbonized sand, it was indicated that up to three pounds of sand would be required to sink one pound of oil. Large-scale applications of amine-coated sands envision spraying the sand in a slurry form from a large vessel or hopper dredge.

In ports and harbors it has been mentioned that turbulence or agitation of the water body caused by storms or passing vessels may tend to release oily masses previously sunk. For siliconized sand, it has also been suggested that one per cent bone flour or an inexpensive fertilizer may be added to promote bacterial growths and accelerated decomposition of the sunken mass.^(2,4) Table I summarizes the types, application rates and relative costs of various sinking agents.

IV FIELD EXPERIENCE

The most prominent large-scale application of sinking agents was that undertaken by the French to sink large masses of TORREY CANYON oils in the Bay of Biscay. Some 3,000 tons of calcium carbonate (blackboard chalk from the Champagne area of France) coated with about one per cent sodium stearate, was used to treat and sink about 20,000 tons of floating oils, although this amount was never precisely defined. The powdery chalk was sprayed or sprinkled over the thick, highly viscous and weathered oil patches and thereafter the water surface was mixed by vessels criss-crossing the area. The oil-chalk mixture reportedly sank in about 60-70 fathoms of water. The area of sinking was

known to partially cover scamp fishing grounds and thus there was fear of bottom inundation and oil resurfacing. Numerous observations, since this incident, however, have reported no adverse effects upon fisheries and bottom life, and there have been no sightings of resurfacing oils upon the water or adjoining shorelines. Nevertheless, it was concluded that lack of knowledge on the precise fate of the oil shows need for further trials before this method may be recommended in other situations. (11,13,14,15,16,17)

Opinion still remains divided on the use of oil sinkants as to their efficiency, cost, application, and possible adverse effects. With sinking agents, the same problems are encountered in the application and distribution as was indicated in the lecture on floating sorbents. However, with sinking agents, operational logistics become increasingly more difficult because of the much larger amounts of material required for treatment.

Although damaging effects have been ascribed to toxicity and smothering of bottom life by sunken oils, the sinking approach serves to localize oil pollution, to prevent its spread over the water surface, and theoretically submerge and anchor the oil near the source of pollution. Considering that the bottom of harbors and bays near many industrial ports are grossly polluted and nonproductive, emergency sinking of oils in these areas may not increase damage to fisheries. Dilution by flowing waters in certain areas may also be sufficient to adequately

TABLE I - OIL SINKING AGENTS, APPLICATION RATES AND OTHER OPERATIONAL DATA^A

Type Material	Application Ratios (Weight Sinking Agent: Weight Oil Treated)	Comments
Silica, untreated		Released oil easily after sinking
Carbonized sand	1:1 to 3:1	Higher proportion of sinking agent considered most appropriate; \$27/ton carbonized sand (1948); specific gravity particles = 2.7
Sands, amine-coated	3.2 to 2:1	Large-scale application costs estimated \$5 - \$10 per ton of oil treated
Sands, 0.5% silicone coated		More effective on heavier oils
Fly ash, untreated		Released oil easily after sinking
Fly ash, 0.5% silicone coated	2:1 ratio or higher	Permanent oil sinking reported; more effective on lighter oils.
Spent tannery lime		Good oil retention properties after sinking
Kaolin clay		Released oil easily after sinking
Bentonite, montmorillonite clay, treated and untreated		
Calcium carbonate		Released oil easily after sinking
Fuller's earth	1:1 to 9:1	1:1 to 3:1 for sulfurized oil; 3:1 to 9:1 for desulfurized oil.
Calcium carbonate - Champagne chalk treated with 1% sodium stearate	Approx. 1:1	Used off the coast of France during the Torrey Canyon; \$60 - \$80/ton sinking agent. Specific gravity particles = 2.7.
Synthetic silicate		High efficiency in absorbing fuel and crude oils, some difficulty in sinking the mass.
Synthetic plus filler material	4:3 or higher	Estimated \$120/ton sinking agent.

^ABibliography (2, 3, 4, 9, 10, 12, 13, 14)

minimize toxicity to nearby shellfish grounds. The other important point of view is that sinking agents, even if used in harbor areas because of fire or explosion danger, can at best be of temporary benefit. The resurfacing oils, although less objectionable due to weathering, may require pick up. Furthermore, sinking may greatly extend the period over which aquatic fauna and flora are affected. (1,2,8,12)

V R & D PROGRESS

Dutch Shell Laboratories, Holland, (11) was one of the first groups to really evaluate sinking agents on a field scale basis. Their studies, still underway, involve using sand treated with an amine. One very important finding from their investigations was that there was a correlation between clay content and performance as measured by the percentage of oil sunk. The lower the clay content the more efficient the sinking agent. The Warren Spring Laboratory, United Kingdom, (6) impressed by the results of these studies, conducted similar field investigations during 1969. Conclusions reached by the Warren Spring Laboratory were as follows:

- 1 The sinking was not as effective as first hoped and it would appear that the thickness of the oil film is an important factor. Nevertheless, between 50 and 70 per cent of the oil put on the sea was sunk.
- 2 The skin divers reported that the oil sank to the bottom in small particles which were only slightly more dense than the sea. Consequently, the tidal current along the sea bed was sufficient to carry the oil over the ripples of sand on the bottom.

- 3 Trawling was carried out and although no actual lumps of oil were collected, sufficient oil was rubbed onto the netting of the trawl to foul both the catch and the fishermen when they were pulling it back into the vessel.
- 4 The oil which remained afloat was particularly difficult to dispose of using either more sand slurry or the normal solvent emulsifier mixture agitated by water hoses. Further investigations on this particular phenomenon are being carried out both in England and in Holland.

In the United States, the Army Corps of Engineers, under contract to the U. S. Coast Guard, is evaluating various types of sinking agents -- treated and untreated -- as well as investigating the possibility of using their hopper dredges, normally used for dredging harbors, to handle and apply the sinking agents. Results of these studies should be available in 1970.

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BURNING AGENTS

I INTRODUCTION

Burning of oil on water or land by special methods and materials seems to offer an attractive and perhaps inexpensive means of eliminating large amounts, providing of course, the many significant hazards are also recognized. Freshly-spilled oils and crudes containing volatile components are relatively ignitable. If a thick layer of oil on water is present, the oil will sustain burning until the volatiles and a portion of the heavier fractions are combusted. Conversely, with fresh oil spills within a harbor or confined area, a significant fire danger exists when the level of hydrocarbon vapors is within the range of flammability, (e.g. gasoline, aviation fuels, or light crude oils) (2, 8, 19 - see references in "Sinking Agents" lecture).

Wood, debris or other material caught within an oil slick can serve as a wick to start or sustain an oil fire. The cooling of a layer of oil by the water body beneath will greatly deter burning. However, the wick will withdraw the oil and insulate the burning oils from the cooling action of the water, and at the same time provide a renewal and vaporization surface for combustion.

II EXPERIENCE ON WATER

A General

Experience by certain investigators has indicated that floating oils on the sea with thicknesses less than 3 millimeters (0.12 inches) will not burn. It is also reported that layers of

kerosene, gas oil, lubricating oil and fuel oil on water will not burn at all without a wick. In one instance, attempts were made to ignite fresh Iranian crude oil five minutes after a spill without success. Once an oil spillage has spread, the material quickly loses its volatile components and ignition is extremely difficult. Weathered oils are consequently reported to present almost no fire hazard. (2, 3, 8, 19 - see references in "Sinking Agents" lecture)

B EPA Lab Experiments

In experiments carried out at the Edison Laboratory, a heavy fuel oil and a light-weight crude oil were placed atop a layer of water contained in metal tanks with 24-square-feet of exposed surface area. Attempts were made to combust the oils using different burning agents. It was concluded from these experiments that the light crude, freshly applied in a floating thickness of 2.5 millimeters (0.1 inches), required external support with burning agents and an ignition source to burn near completion.

When the No. 6 fuel was used for testing, one of the agents used would not sustain burning at a thickness of 1/2 to 2/3 inches. Another agent generously applied over the surface of the No. 6

fuel caused sporadic burning and the minimum required oil thickness to sustain burning was 1/3 to 1/2 inches. It is important to note that a thickness of 1/3 to 1/2 inches is equivalent to an oil slick of 7 million gallons/sq. mile. It was evident after this burning that appreciable oil was still remaining. A third agent used performed well with the No. 6 fuel at a thickness of 1/10 to 1/4 inches. The manufacturer producing this material, however, suggests that in order to have complete burning of all the oil, the oil layer must be completely covered with the material with no broken patches. Required amounts of this material (very low bulk density) may be as high as one pound for each 12-15 square-feet of oil slick. (1, 3 - see references in "Sinking Agents" lecture)

C EPA Field Tests

Field scale oil slick burning experiments, with and without special agents have been undertaken in 1970 by both the U. S. Navy and the Edison Water Quality Laboratory. Preliminary data from these experiments indicate the following:

- 1 Burning of free floating or uncontained oil slicks is extremely difficult unless the thickness of oil is 2 mm or greater.
- 2 Adequate automated seeding methods for both the powder and nodule-type burning agents are lacking. Spreading of the burning agent on the oil slick had to be accomplished by hand. This conclusion was also reached by the Navy, which conducted burn-

ing experiments in May 1970.

- 3 Contained South Louisiana crude oil was successfully burned - 80% to 90% reduction - without the application of burning agents and/or "priming" fuels. Bunker C could not be ignited under these same conditions.
- 4 Bunker C was successfully burned - 80% to 90% reduction - when the slick was seeded with burning agents and an appropriate priming fuel. It was discovered that South Louisiana crude oil performed better as a priming agent than did gasoline or lighter fluid.
- 5 Use of magnesium type flares and gasoline torches to ignite the burning-agent-treated slick proved unsuccessful. Success was achieved, however, using a blow torch once we learned how to manipulate the torch in such a manner that the torch gas pressure did not push aside the oil and seed material so as to expose the water surface.

D U. K. Experience

Burning agents were considered when the TORREY CANYON was in the final stages of destruction off the British coast in March of 1967. As a last resort, the British Government attempted simultaneous and complete burning of the 15,000-20,000 tons

of oil remaining in the badly broken tanker by aerial bombing, incendiaries, and catalyst-oxidizing devices. The major objective was to penetrate and lay open the decks by "explosive surgery," exposing the oil in the storage compartments to large amounts of oxygen required for burning. High-explosive, 1,000 pound bombs filled with aluminum particles, thousands of gallons of aviation fuel, napalm bombs, rockets, and sodium chlorate devices served to produce a mass fire, if not a sustained fire. The British concluded that no appreciable amounts of oil escaped burning, but if any did, it was lost to the open sea. (13, 14, 18 - see references in "Sinking Agents" lecture)

E Use Considerations

Controlling the burning oil mass and ensuing air pollution problems would appear to preclude intentional burning except where the oil mass is distant from the coastline, offshore facilities, vessels, etc. The safety and welfare of all parties however remote from the burning site are of utmost importance. The possible loss of additional oil, and the loss of a drilling platform or vessel at the source of the spill must be recognized. Because of potential merits in controlled burning, further research is desired on new methods, techniques and procedures both in the laboratory and in the field, together with additional guidelines for burning.

III EXPERIENCE ON LAND

J. Wardly Smith, Ministry of the Envi-

ronment, United Kingdom, has conducted a series of research experiments involving the burning of oil on beaches. The conclusions reached by these studies were:

- 1 The type of heavy oil normally contaminating beaches and the foreshore is very difficult to burn by ordinary means and combustion ceases when the source of heat is removed.
- 2 The addition of solid oxidants aids the combustion of part of the deposit, but a sticky, tarry residue is left with medium heat and a residue of dry, black carbon with prolonged intense heat. About 30 per cent by weight of oxidant has to be employed to achieve this and when the deposit occurs on sand, shingle or pebbles the amount of heat necessary to raise the whole to ignition temperature is so great that, in practice, the cost of removal would probably be excessive.
- 3 The application of an oil-absorbent, combustible material, such as sawdust impregnated with an oxidant, resulted in a much steadier burning rate and an increased removal of the deposit. The additive, however, burns away before the higher-boiling, tarry fractions begin to burn.
- 4 Although some improvement was obtained by adding materials which function as a wick, the same limitation regarding the amount of heat to be supplied still operated.
- 5 A major disadvantage of burning as a method for the removal of oil

deposits on beaches, especially when dealing with the large semi-solid lumps, is that, when heat is applied, the oil becomes mobile and penetrates deeper into the beach, thus increasing the contaminated area if it becomes exposed at a later date.

- 6 On the basis of these small-scale experiments it was considered that, for all practical purposes, burning beach oil deposits would be less efficient and more costly than mechanical or manual removal, and that further investigation would be unprofitable.

IV COMMERCIAL BURNING AGENTS

Commercial burning agents are available for promoting combustion of an oil slick. However, in most cases it is apparent these agents are designed for a relatively thick oil layer which is sufficiently contained. These agents are intended to serve one or more functions such as providing increased surface area exposed to burning; addition of catalysts, oxidizers and low-boiling volatile components; absorbence and entrapment of the oil; or creating a wicking mechanism via surface diffusion and capillary action by the material added.

To the best of our knowledge, burning agents are available from only four sources:

- 1 Eduard Michels GmbH, 43 Essen, Postfach 1189, Ruttenscheider Str 1.: "Kontax", the commercial name for this agent, ignites spontaneously when it comes in contact with water. In 1969 the Dutch conducted field experiments which included burning of oil on beaches, and in open waters. Results of this investigation indicated that

the quantity of "agent" required was dependent upon wind, condition of sea and continuity and thickness of oil.

Dutch engineers also reported that a method should be developed to jettison, hurl or catapult the "agent" from a vessel in such a way that there is not the slightest risk of having the "agent" come in contact with rainwater or spray. Dropping from an airplane is worth considering provided special packaging requirements are met.

- 2 Pittsburgh Corning, One Gateway Center, Pittsburgh, Pa.: Known as "SeaBeads", these cellulated glass nodules are available in sizes from 1/8" to 1/4" in diameter. By capillary action, the nodules become coated with oil. Depending upon the type and age of the spilled oil, combustion is accomplished by using an incendiary device alone, or in combination with a "primer fluid" such as gasoline. After burning, SeaBeads still remain, therefore, they must be collected or left to break up by abrasion. During the "Arrow" incident in 1970, this burning agent was used, with varying degrees of success, on small patches of spilled oil.

- 3 Guardian Chemical Corporation, Long Island City, N. Y. 11101: Pyraxon, a powder material, is a catalyst containing small amounts of oxidizing materials. Pyraxon liquid is used as the priming agent or starter fluid, with the powder being sprayed, blown or dropped onto the oil, in and around the flame.

- 4 Cabot Corporation, 125 High Street, Boston, Mass.: Cab-O-Sil ST-2-0 promotes combustion by acting as a wicking agent. Produced from fumed silica, this powdery-like material, is surface treated to render it hydrophobic. It may be applied directly to the slick or by spraying in a stream of water. Combustion is best accomplished by using an incendiary device in conjunction with a "primer fluid". Reportedly, this product was used successfully for handling a 2,000 gallon spill at Heard Pond, Wayland, Mass.

This outline was prepared by R. T. Dewling, Director, Research & Development, Edison Water Quality Laboratory, Edison, N. J. December 1970.

GELLING AGENTS

I INTRODUCTION

Gelling agents are applied over the surface or periphery of a floating oil slick and are intended to absorb, congeal, entrap, fix, or make the oil mass more rigid or viscous so as to facilitate subsequent physical or mechanical pick up. The gelling concept is also undergoing extensive study for stabilizing petroleum cargoes aboard a stranded or heavily-damaged tanker at sea subject to mass spillage.

II TYPES AND COST

Possible gel agents include molten wax or soap solutions, lanolin, liquid solutions of natural fatty acids, soaps of the alkaline metals, treated colloidal silicas, the aminoisocyanates, and the polymer systems. One manufacturer indicates a cost of \$3 per gallon of gel agent, a use ratio of about 1:1, and the ability to mix the recovered gel mass with fuel oils serving as replacement bunker fuel. This gel agent is applied to the surface of the water by a high-pressure spray system to provide sufficient agitation and mixing of the gel-oil mass.

III R & D Findings

Preliminary research on the gelling of tanker cargoes tends to show that a 3-10 percent gel agent will be required at a materials cost of 13-40 cents per gallon of tanker crude oil gelled. However, total operational costs, and the ability to salvage and reuse the gelled cargoes, are not fully known at this time.

The gelling approach for treating oils on

water, although promising, must provide greater attention to application and distribution, lower materials and operational costs, and suitable means of picking up the amorphous oily masses. Bunker C, heavy crude oils, and some gel agents by themselves may clog intakes, pumps and suction lines. The major difficulty is the ability to harvest the congealed mixtures since gelled oils cannot be easily collected by mechanical or manual means. Necessary improvements are needed in the gelling approach in line with a total operational systems cleanup. (1, 2, 3, 8 - see lecture on "Sinking Agents" for these references)

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This outline was prepared by R. T. Dewling, Director, Research & Development, Edison Water Quality Laboratory, Edison, N. J. December 1970.

SORBENTS

I INTRODUCTION

A. Sorbents are oil spill scavengers or clean-up agents which adsorb and/or absorb oil. Based on origin, sorbents may be divided into three general classes:

1. Natural products.
2. Modified or chemically-treated natural products.
3. Synthetic or man-made products.

B. Sorbents may be further classified as to their physical characteristics:

1. Powdery products.
2. Granular products.
3. Fibrous materials.
4. Pre-formed foam slabs or sheets.

II TYPES OF SORBENT PRODUCTS

A. Types of floating sorbent materials presently available are:

1. Natural Origin: Types derived from vegetative sources comprise straw, hay, seaweed, kelp, ground bark, sawdust, reclaimed fibers from paper processing, and peat moss. Types derived from mineral sources may include the various clays, including montmorillonite, kaolin, fuller's earth, diatomaceous earth,

etc.; vermiculite and the other micas; many forms of silicates; perlite; pumice; and asbestos. Sorbents of animal origin include chrome shavings from leather processing, wool wastes, feathers, and textile wastes.

2. Modified Natural Products: These materials comprise most of the sorbent types mentioned above but are chemically-treated to produce a more desirable result. Some of the modified types are expanded perlite, charcoal, stearate-coated talc, asbestos treated with surfactant, and sawdust and vermiculite coated with silicones.

3. Synthetic Products: These sorbents include a vast array broadly categorized as plastics and rubber, but more specifically as the ethylenes, styrenes, resins, polymers and co-polymers.

III SORBENT CHARACTERISTICS

A. Desirable Sorbent Characteristics

1. Oleophilic - has greater attraction for oil than water.
2. Hydrophobic - repels or rejects water.
3. Adsorbtive - oil will adhere to the surface of the material.

4. Absorbptive - oil is assimilated into the material.
5. High oil capacity - the ratio of oil picked up to material applied (lb/lb) should be at least 5:1 but preferably 10:1 or greater.
6. Retentive - leaking of oil from material should be minimal after harvesting.
7. Low costs - on a non-reusable product. High initial costs are acceptable for reusable products.
8. Products should float under all conditions.

Presently, none of the existing products have all of these desirable qualities.

IV OPERATIONAL ADVANTAGES AND DISADVANTAGES

A. Advantages

1. Aids in removing oil from water surface and alleviates or precludes undesirable after effects.
2. Minimizes and decreases spread of oil.
3. Generally, inexpensive and available in large quantities.
4. Non-toxic.
5. May increase both performance of booms and skimming techniques.
6. Minimizes shore pollution when beached.

B. Disadvantages

1. No effective workable system at present.
2. High labor costs associated with acquisition, transportation, stockpiling, deployment, distribution on and working into an oil slick, retrieval and ultimate disposal.
3. Manual retrieval only practical under calm conditions.
4. Some products interfere with other forms of physical removal by clogging skimming and suction devices.
5. Pollutional problems on disposal.
6. Some sorbent products ultimately sink.

a. As their true density is greater than water, certain mineral products sink when air entrained in capillaries is replaced by oil and/or water or when products are wetted by water.

b. Some natural vegetative products such as straw, sawdust or waste pulp fibers become waterlogged upon prolonged exposure in water and may sink.

V SORBENT USES

- A. Sorbents may be used for many reasons

- 1 To agglomerate oil from a massive spill to minimize spread and potential damage. The above could be applicable to spills on large open bodies of water where other control procedures are ineffective and in other areas where presently available control procedures would be effective but are not readily available.
- 2 To "polish" a slick remaining after other control procedures such as booming and skimming have removed most of the oil.
- 3 To sorb free oil from contaminated surfaces to facilitate cleanup procedures.
- 4 To deploy sorbents onto open waters and clean beaches in anticipation of the arrival of an uncontrolled slick.
- 5 Used in conjunction with either fixed or towed booms.

VI SORBENT EFFECTIVENESS

- A To define sorbent effectiveness certain basic questions relating to the environmental use of sorbents under actual spill conditions must be considered.

- 1 Why were sorbents used?
- 2 What procedures will be used to harvest the oil-

sorbent mass?

In each of the situations listed in Section VI, the effectiveness must be evaluated differently because criteria for evaluating effectiveness must be related to the original objective for each different use.

For instance, the cost/application ratio (i.e. product costs/unit of oil sorbed) may be of primary importance in selecting a product for agglomerating a massive spill but would be of a lesser degree of importance for "polishing" action or for alleviating or minimizing potential damage.

VII SORPTION PROCESSES

- A The accumulation of oil by sorbent products is a complex phenomenon dependent upon several physical processes. For example, when straw is used the different processes must probably occur as follows:

- 1 Adsorption of oil to the straw surface.
- 2 Absorption of oil into the interstitial fibers and filtration into the hollow stem.
- 3 When saturation is reached

additional oil is picked up by oil to oil cohesion.

B Products have different adsorptive and absorptive capacities. For example, for free flowing oils:

- 1 A highly pulverized mineral product manifests primarily adsorption. The pickup capacity is related to the surface area available.
- 2 A polymeric foam product manifests primarily absorption because of its high internal porosity.
- 3 The extraneous oil pickup of all products is related to the viscosity of the oil to be sorbed. The higher the viscosity, the greater the oil to oil cohesion and adhesion.

VIII USING SORBENTS EFFECTIVELY

A On unconfined oil slicks

- 1 Products should be uniformly applied to the slick. Most unconfined oil slicks thin out very readily. Therefore, in order not to waste product, a thin uniform layer is preferred.
- 2 The effectiveness of most products is increased by ultimately mixing the product into the oil slick. This can be accomplished:
 - a By churning up the mass by running boats through at high speed after broadcasting of products.

b By towing netting stretched between boats through the mass at slow speed.

c By existing environmental energy such as wind, wave and current action.

d If the above is not feasible, a time period of at least 3-6 hours should be allowed for the oil and product to mix. Most spills occur in tidal areas, and as such, the change of tide produce a minimum mixing energy. Additionally, the weight of most sorbent products will be sufficient to work the product into the oil if sufficient time is allowed.

e A harvesting procedure utilizing netting or booms which encircles a given area and concentrates the oil/sorbent mass by decreasing the area is also effective.

IX OIL CAPACITY AND COSTS OF SORBENTS

A Presently, there are no standard tests for evaluating the effectiveness of sorbents. However, small scale laboratory testing of many products have been completed which at least give a measure of the relative oil capacity of many available products.

B Table I summarizes the results

of bench scale testing of the oil sorbing capacity of selected products. The data was summarized from Edison Water Quality Laboratory tests, the oil pollution literature and manufacturers' brochures.

- C Table I reflects product costs varying from \$20 to \$20,000 per ton which breaks down to costs of approximately \$0.02 to \$1.00 per gallon of oil sorbed. These costs are product costs only, based on the reported oil capacity of the products. They do not reflect the equipment and labor costs associated with their use in the environment.

- D Compared with other oil spill cleanup techniques such as booming, skimming, dispersing and sinking, cleanup with sorbents is reportedly the most costly procedure. The costs vary from \$0.50 to \$5.00 per gallon of oil picked up, depending on the size of the spill and the equipment utilized. In the absence of an effective system for utilizing sorbents under actual spill conditions, the high cost are a reflection primarily of the labor costs of the multi-step process.

X LARGE SCALE SORBENT TESTS

E. A. Milz⁽²⁾ of Shell Pipeline Corporation, Houston, Texas, reported the performance of 15 floating sorbents tested on a relatively large scale.

- A Summary of test data is presented in Table II.

B Conclusions from tests.

- 1 Tests showed that pound for pound polyurethane and urea formaldehyde foams are the best oil sorbents. On a weight basis these materials removed about 10 times more oil than other sorbents tested.
- 2 For long contact times the quantity of oil sorbed is primarily a function of oil viscosity and density.
- 3 In most cases sorbents lose oil after pickup by drainage and evaporation. About 80% of oil initially absorbed will be retained after draining for 24 hours.
 - a One exception to the above is Kraton rubber which dissolves oil into the body of the material and completely retains it. To facilitate sorption, samples were granulated to a particle size of 4 mm. Kraton rubber may also be foamed which should improve sorption.
- 4 Power mulching machines can effectively spread up to nine tons of straw or hay per hour with immediate mixing with oil. In contrast, when hay was simply dumped overboard,

it remained in large dry clumps for over half an hour even in 4-5 foot waves.

- 5 Power mulchers are satisfactory for shredding and spreading polyurethane foams.
- 6 When sorbents are used with booms the same problems are encountered as by containment of oil alone by booms. Wave action will cause spill-over and currents above 1 fps will cause under-sweep.
- 7 Nets are more effective than booms for containing relatively small quantities of stringy material such as hay, bark and shredded foam. With 1-inch mesh nets, velocities of 2-3 fps are possible for small quantities of material without product loss. For large quantities of material, velocities of 1-2 fps are possible without failure (Figure 1).
- 8 All collection or harvesting processes for oiled sorbents on open water involve screening processes. Therefore, the selection of mesh size for harvesting devices is critical and is related to the sorbent particle size.

XI POTENTIAL OF SORBENTS

- A Because of the inherent limitations or regulatory restrictions for such techniques as booming, skimming, sinking, dispersing, burning or gelling, the advantages of sorbent systems for cleaning up

oil spills show great promise.

- B Reusable high-oil capacity sorbent products used in conjunction with self-contained mechanized systems will be developed which will have the following desirable features:
 - 1 Recovery of oil which decreases problem of disposal. The recovered oil can be taken to a separator and incorporated into refinery feeds rather than buried.
 - 2 Products will be reusable. Certain poly-foam products have an initially high-cost which decreases geometrically for each subsequent re-use. Such products may be used dozens of times and potentially hundreds of times by reinforcement of product with plastic netting.
 - 3 On open waters under inclement conditions there is no expediency for harvesting. The products may be beached and subsequently the oil and product recovered on the beach or gathered later under calm conditions from the water surface.
- C Costs will decrease as manual labor is replaced by mechanical equipment incorporated into continuous self-contained systems.
- D Presently the FWQA, U. S. Coast Guard and the A.P.I. are evaluating proposed sorbent systems submitted for research funding.

TABLE I

COSTS OF SORBENTS (1)

(Product costs per 1,000 gallon spill. Does not include labor and equipment costs)

Type Material	Pick Up Ratio Weight Oil Pick Up Weight Absorbent	Unit Cost Absorbent \$ (Ton Absorbent)	\$ Cost of Absorbent for Cleanup of 1,000 Gals. Oil Spill ^B
Ground pine bark, undried	0.9	6	27
Ground pine bark, dried	1.3	15	47
Ground pine bark	3	---	---
Sawdust, dried	1.2	15	50
Industrial sawdust	---	56	---
Reclaimed paper fibers, dried, surface treated	1.7	30	75
Fibrous, sawdust and other	3	---	---
Porous peat moss	1.0	---	---
Ground corncobs	5	30	21
Straw	3-5	30	27
Chrome leather shavings	10	---	---
Asbestos, treated	4	500	440
Fibrous, perlite, and other	5	416	290
Perlite, treated	2.5	230	320
Talcs, treated	2	70-120	120-210
Vermiculite, dried	2	---	---
Fuller's earth	---	25	---
Polyester plastic shavings	3.5-5.5	100	80
Nylon-polypropylene rayon	6-15	---	---
Resin type	12	3,100	900
Polyurethane foam (1)*	70	20,000	1,000
Polyurethane foam (2)	15	4,500	1,050
Polyurethane foam (3)	70	---	---
Polyurethane foam (4)	40	2,260	195
Polyurethane foam (5)	80	1,200	55

*Numbers refer to different types.

TABLE II

LARGE SCALE SORBENT TESTS(2)

Test Conditions: Sorbent applied to oil slick confined to 20' x 20' area, no mixing

Sorbent Material	Quantity Used (lbs.)	Test Oil		Test Time (hrs.)	Oil Removed (lbs.)	Oil to Sorbent Ratio
		Thickness (in.)	Quantity (lbs.)			
Kraton 1101	25	1/4	700	24	28	1.1
Kraton 1107	25	1/4	700	24	ca. 30	1.2
Urea Formaldehyde 2" x 24" x 60"	1.6	1/4	700	24	41	26
Polyurethane (1)	20	1/4	556	2	560	28
Polyurethane (2)	20	1/4	660	1	100	5
Polyurethane (3)	5	1/4	300	5	230	46
Ekoperl	24	1/4	300	24	120	5
Hay (4)	49	1/4	700	24	210	4

1. Fine ground polyurethane (ca. 1/4" diameter). For this test there was insufficient oil present to saturate the polyurethane. There was no trace of oil left after removing the polyurethane.

2. Polyurethane in 9-foot long by 2-foot diameter bag. The bag picked up over 500 pounds of water and only 102 pounds of oil.

3. Scraps of polyurethane of 1 and 2-inch thickness in various shapes and sizes up to 1-foot by 4-feet.

4. Performance of straw and bagasse are similar to hay.

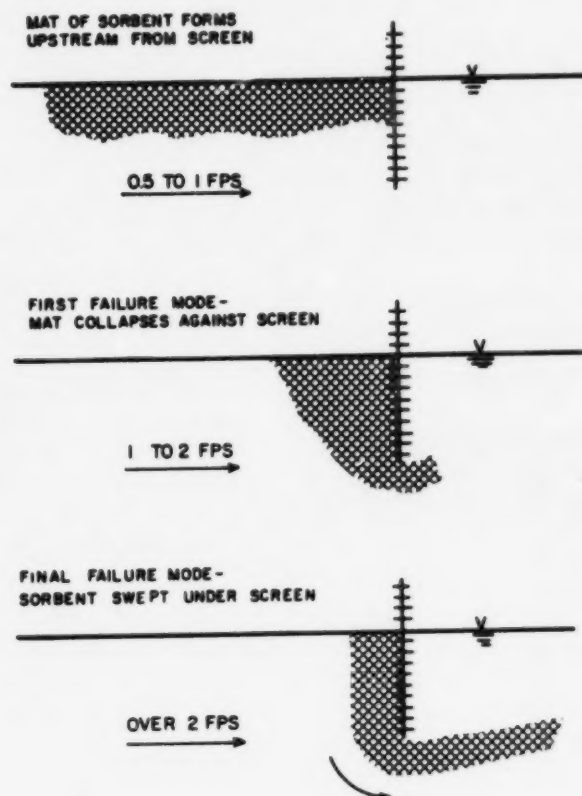


Fig. 1 - Sorbent Barrier Failure Modes in Current

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- 1 Struzeski, E. J. and Dewling, R. T., Chemical Treatment of Oil Spills. Published in Proceedings Joint Conference (API/FWPCA) on Prevention and Control of Oil Spills, New York, December 1969.
- 2 Milz, E. A., Oil Spill Control Equipment and Techniques. Presented to the 21st Annual Pipe Line Conference, Dallas, Texas, April 14, 1970.
- 3 Study of Equipment and Methods for Removing Oil from Harbor Waters. Prepared by Battelle Memorial Institute, Richland, Washington for U. S. Navy, Civil Engineering Laboratory, Port Hueneme, California, August 1969.
- 4 Combating Pollution Created by Oil Spills. Prepared by A. D. Little, Inc. for Department of Transportation, U. S. Coast Guard, June 1969.

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BOOMS

I INTRODUCTION

In spite of everyone's best efforts at prevention oil has been, and will continue to be spilled on the water. What do you do about it once it's there? From other information presented in this training manual you know that, if ignored, it won't go away. It may move away from the area where it was deposited, but if left in or on the water, something will be adversely affected by it. If you are the party responsible for the loss, it is a violation of federal law, Section 11 (b)(3), of the Federal Water Pollution Control Act, as amended (84 Stat. 92 33 USC 1161) not to report the oil loss, and after you report it, it will be to your advantage to do something about it. If you are a pollution control official or have delegated responsibilities in this area, you also will want to do something about it. But what?

The first priority in your control program is to attempt to limit the spread of the oil mass. Experience has shown that if left to its own devices, oil spreads into thinner and thinner films and breaks apart into smaller patches covering larger areas. The greater the area covered the more difficult and costly the cleanup program becomes. As the oil mass spreads, resources such as municipal, industrial, and agricultural water supply sources; waterfowl, fish and general aquatic flora and fauna; recreational interests, both public and private, as beaches, shorefront properties and homes, marinas, pleasure boats and tourist centers; and shellfish harvesting, to name a few, may be affected. To contain an oil spill within a limited area, oil retention barriers commonly called "oil booms" have been developed. A satisfactory boom design has to overcome the many forces acting upon it.

Forces are exerted by the oil being contained, and the water in which it is immersed. The boom may be used to encircle an oil slick to prevent its spread, to encircle an oil slick and then compact it so as to decrease the area of coverage and increase film thickness to make recovery easier, or to keep the oil away from sensitive areas. It is an essential tool in any oil pollution control program and generally will be the first piece of equipment placed on scene and the last removed. Considering its importance, an understanding of the way the barrier functions, and the limitations of different designs, is essential.

II CHARACTERISTICS OF OIL ON WATER

In order to understand the forces acting on a boom being used to contain oil in the water environment, it is first necessary to understand those forces acting on the oil itself. When oil is spilled on water, it generally tends to spread outward on the water surface forming a thin continuous layer or, depending on conditions, it may tend to accumulate as a slick having some particular thickness. How it will spread depends on the surface tension of the water, the surface tension of the oil, and the interfacial tension between the oil and water. The tendency to spread is the result of two physical forces: the force of gravity and the surface tension of the water on which the oil has been spilled. The horizontal motion of the oil slick is caused by outward pressure forces in the oil which are a direct result of the gravitational force. Of the forces acting, gravity and surface tension will tend to increase the spread of an oil film while inertia and viscous forces tend to retard it.

The spreading tendency will be increased by waves, wind, and tidal currents. In general the spread resulting from these random motions will be smaller than those caused by tension and gravity forces. It must also be recognized that the character of oil when spilled on water does change with time, but generally the properties which are important to spreading, namely, density, viscosity and the surface and interfacial tensions, change slowly and, therefore, can generally be predicted.

The equations which follow define only what the diameter of an oil slick would be if it remained as an integral mass after loss. The oil mass may be transported to different locations by wind, tide or current conditions, while still spreading. If the situation is such, however, that the slick is broken apart into many smaller components, these equations may only be applied to each integral component as there is no acceptable way of accurately predicting the total area which might be covered by individual oil masses other than actual field observations.

For the situation in which a quantity of oil is spilled into the aquatic environment within a short time frame (not a slow continuous discharge), the following series of equations may be used to predict the diameter of the oil slick (l in feet) after a specified time (t in seconds).

The symbols used in the following equations may be defined as follows:

- l - diameter of the oil slick in ft.
- t - time in minutes from entry of oil into the aquatic environment for which size is required
- v - volume of oil spilled in gallons
- g - gravitational constant

$$32 \text{ ft/sec}^2$$

γ - kinematic viscosity of water

$$10.7 \times 10^{-6} \text{ ft}^2/\text{sec}$$

σ - net surface tension of oil (typical order of magnitude

$$20.6 \times 10^{-4} \text{ lbs/ft (30 dynes/cm))}$$

ρ - difference in mass density between water and oil (typical order of magnitude

$$3.12 \text{ lbs/ft}^3)$$

Situation 1

The time period within 1 hour after the spill occurs when gravity and inertia forces are important:

$$1 = \left[(\Delta g)(v)(0.13)(t^2)(60)^2 \right]^{\frac{1}{4}}$$

Substituting typical values for constants -

$$1 = 11.1 \left[(v)(t^2) \right]^{\frac{1}{4}}$$

Situation 2

The time period from 1 hour to 2 hours after a minor spill, from 1 hour to 24 hours after a moderate spill, and from 1 hour to 48 hours after a major spill when gravity and viscous forces dominate:

$$1 = \left[\frac{(\Delta g)(v^2)(0.13)^2(t^{\frac{3}{2}})(60)^{\frac{3}{2}}}{\gamma^{\frac{1}{2}}} \right]^{\frac{1}{6}}$$

Substituting typical values for constants -

$$1 = 6.53 \left[v^2 t^{\frac{3}{2}} \right]^{\frac{1}{6}}$$

Situation 3

The final phase when surface tension is balanced by viscous forces:

$$1 = \left[\frac{(\sigma^3)(t^3)(60)^3}{\rho^2 \gamma} \right]^{\frac{1}{4}}$$

Substituting typical values for constants

$$\bar{l} = 9.66 \left[\frac{v}{t^3} \right]^{\frac{1}{4}}$$

Figure 1 illustrates the application of these 3 equations to the special case of a 10,000 ton oil spill. The 3 situations are clearly illustrated. It must be remembered that values calculated are only general approximations as they are based on order of magnitude estimates.

The thickness in inches (h) of the spill may be computed at any time by the equation:

$$h = \frac{v (0.13)}{l^2 (12)}$$

or

$$h = \frac{v}{l^2} (0.011)$$

Situation 3 describes a growth pattern which is independent of the volume v of the oil spill. This is possible as the thickness of the slick is no longer of importance in considering the major forces involved.

When the oil is being discharged from a stationary source at a fairly constant rate, a modification of the above equations is required to estimate slick width (l in ft.) at a specific distance (x in ft.) from the source. These equations may be used to model discharge patterns from sunken or grounded tankers and offshore oil wells.

Additional symbols employed are:

- $\bar{l}$ - width of slick in feet
- $\bar{v}$ - volume flow rate in gal/sec
- x - horizontal distance from stationary source in feet
- μ - current in ft/sec

The situation description for the following is the same as for bulk discharge.

Situation 1

$$\bar{l} = \left[\frac{4.2 \bar{v} (0.13) x^2}{\mu} \right]^{\frac{1}{4}}$$

Substituting typical values for constants -

$$\bar{l} = 1.61 \left[\frac{\bar{v} x^2}{\mu} \right]^{\frac{1}{4}}$$

Situation 2

$$\bar{l} = \left[\frac{4.2 \bar{v}^2 (0.13)^2 x^{\frac{3}{2}}}{\mu^{\frac{3}{2}}} \right]^{\frac{1}{4}}$$

Substituting typical values for constants -

$$\bar{l} = 3.6 \left[\frac{\bar{v}^2 x^{\frac{3}{2}}}{\mu^{\frac{3}{2}}} \right]^{\frac{1}{4}}$$

Situation 3

$$\bar{l} = \left[\frac{0.2 x^3}{\mu^3} \right]^{\frac{1}{4}}$$

Substituting typical values for constants -

$$\bar{l} = 0.449 \left[\frac{x^3}{\mu^3} \right]^{\frac{1}{4}}$$

It should be noted that in the final phases of the spill, the spreading is independent of the volume flow rate.

The force causing the oil to spread may be calculated from the following equation (see Figure 2):

$$F_o = \alpha_w - \left[(\alpha_o)(\cos \theta_o) + (\alpha_w)(\cos \theta_w) \right]$$

Where

F_o - force causing the oil to spread in dyne/cm

α_w - surface tension of the water, (typical order of magnitude 1 dyne/cm)

α_o - surface tension of the oil (typical order of magnitude 30 dyne/cm)

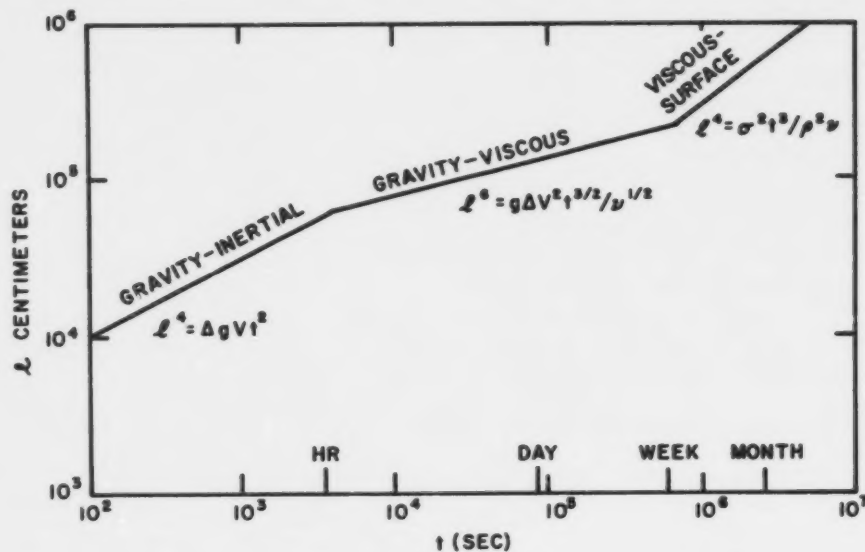


Figure 1 - THE SIZE L OF AN OIL SLICK AS A FUNCTION OF TIME t FOR A 10,000 TON SPILL.

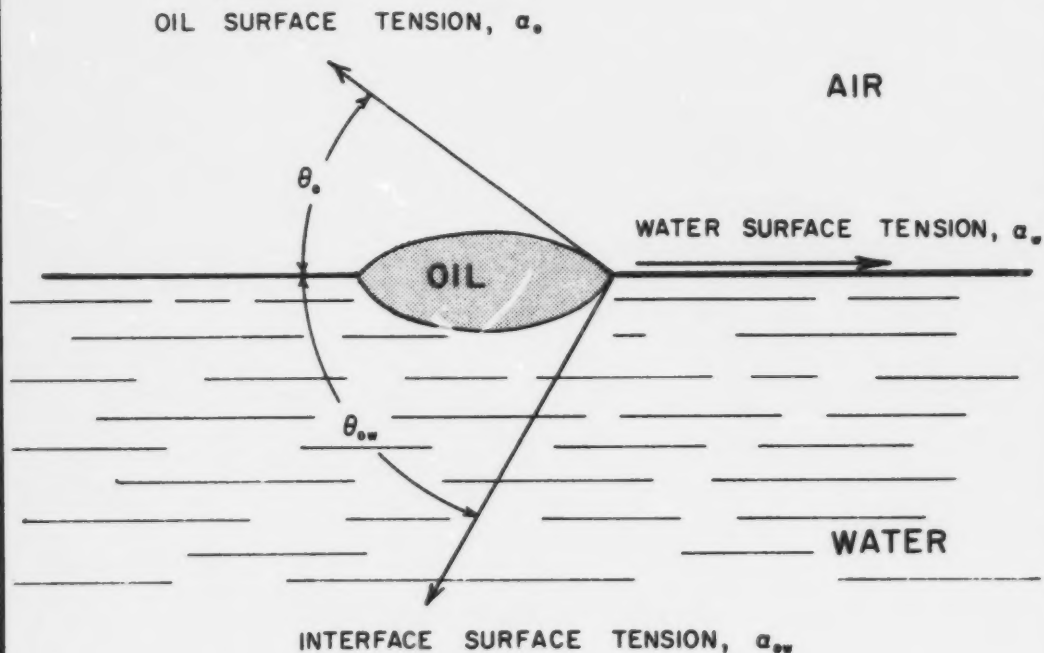


Figure 2 - FORCES ACTING ON AN OIL DROPLET ON WATER.

α_w - interfacial tension in dyne/cm

θ_o - contact angle of oil with water at water surface in degrees

θ_{ow} - contact angle of oil/water interface with water surface in degrees

Although theoretically this force should be considered in boom design, when compared with the other forces acting to cause boom failure in the water environment, it becomes insignificant as will be seen in Section III.

Another characteristic to be considered is that a globule or droplet of oil will have a predictable "rate of rise" as it emerges from an underwater position and rises to the water surface. During the "rise" it is subject to lateral displacement by ocean currents. Large globules of oil (greater than 1 inch in diameter) rise at the rate of approximately 1 foot per second. Smaller droplets rise at about 1.5 feet per second. In placing a containment boom to capture oil either emanating from a submerged source, or falling from a substantial height, the "rate of rise" phenomena has to be considered.

For example:

A tanker has ruptured a line on deck and residual fuel oil is running out of the scuppers to the water 20 feet below. The oil is penetrating into the water to a depth of 15 feet. It will take 15 seconds to rise up to the water surface. There is an ebb tide and the current immediately off of the anchorage is 1 knot. The oil will return to the surface approximately 30 feet down current of the point of entry. A containment boom placed closer than 30 feet to the vessel would lose much of the oil being spilled.

An appreciation of the above concepts is important in understanding why a boom is necessary and how it may be used. It can provide a basis for the spill control officer to develop his own rules of thumb for predicting the physical size of the slick he is going to have to contend with. Coupled with the rule of thumb that a slick will move generally in the prevailing wind direction and at 3% of the wind velocity and taking into account the effect of tide, current and sea state, where applicable, he can begin formulating the plans for his first line of defense.

III FORCES ACTING ON A BOOM

This section will be primarily concerned with defining the reasons why a boom fails. This does not mean physical failure of the boom itself, which is a function of the structural strength of the materials out of which it is fabricated, but rather failure of the boom to contain oil while remaining physically intact. A boom is supposed to be capable of retaining oil slicks; concentrating oil slicks so as to increase thickness; acting as a device to move oil across the surface of the water from point to point; and serving as a diversionary or protection barrier to keep oil out. In almost all cases there is a regrettable tendency to overrate these capabilities rather than underrate them. With present technology, the most satisfactory way of dealing with an oil spill is to contain the oil and then physically remove it as rapidly as possible. The frequent failure of the containment system greatly complicates the physical removal effort.

When a barrier is placed in the path of an oil slick, the spread effect is interfered with and a pool of oil, generally much deeper than that which would result from an undisturbed slick, is formed.

The boom's performance is affected by wind, waves, and currents. It must be capable of conforming to the wave profile so as to maintain its freeboard and have sufficient structural strength to withstand the stresses set up by wave and wind action. Sufficient vertical stability is required to overcome the roll effect forces set up by the water current on the fin and wind on the sail to keep the boom from being flattened out on the water surface. Freeboard (sail) must be adequate to prevent oil from being carried over the top of the boom by wind action and choppy wave motions.

Although wind and wave action are important in boom design, water currents are the usual reason for boom failure. Wind is often the controlling factor in moving a slick about on the surface of the water, and wave motion often contributes to breaking up an integral slick into many smaller patches. The relative current, the resultant of that generated by the water current in the area, be it tidal or river, and the motion of the boom itself, however, will often be the controlling factor in boom failure. Boom failure is defined as a loss of its capability to retain the oil slick.

The following presents a theory, backed by experimental and field results concerning the effects of water currents on oil containment by booms. This information should assist the pollution control officer in selecting the proper depth of skirt and length of boom required in those cases where mechanical barriers appear feasible. The thought should be kept in mind that a mechanical barrier does not have to remain stationary. The relative velocity profile can be changed by allowing the barrier to drift with the oil mass. The failure mechanism can also be modified by instituting skimming

action as soon as possible after the slick is boomed. Quite often, however, the amount of skimming capability available will not be adequate to prevent failure without additional action. The failure characteristics can also be modified by the use of ad/absorbents which will change the thickness profile of the oil in the boom area. An understanding of the failure mechanism provided by the following information is intended to provide a basis for deciding how the boom may best be implemented (fixed containment, drift containment, diversionary use, etc.), and how and when other materials (skimmers, ad/absorbents) might be implemented.

Experimental work has shown that an oil slick being contained by a mechanical barrier will exhibit a shape like that shown by Figure 3. Initial failure will occur when oil droplets break away from the lee side of the head wave. After a critical velocity (u_c) is exceeded, oil droplets will be entrained in the flowing water stream. Unless the droplets have sufficient time to rise through the water and rejoin the slick in Region I, II, or III, they will be swept under the barrier.

Region I is the critical area for defining the limits for oil breakaway. The type of configuration which the oil mass assumes in this region is similar to a gravity wave. The thickness of the oil may be found from the equation:

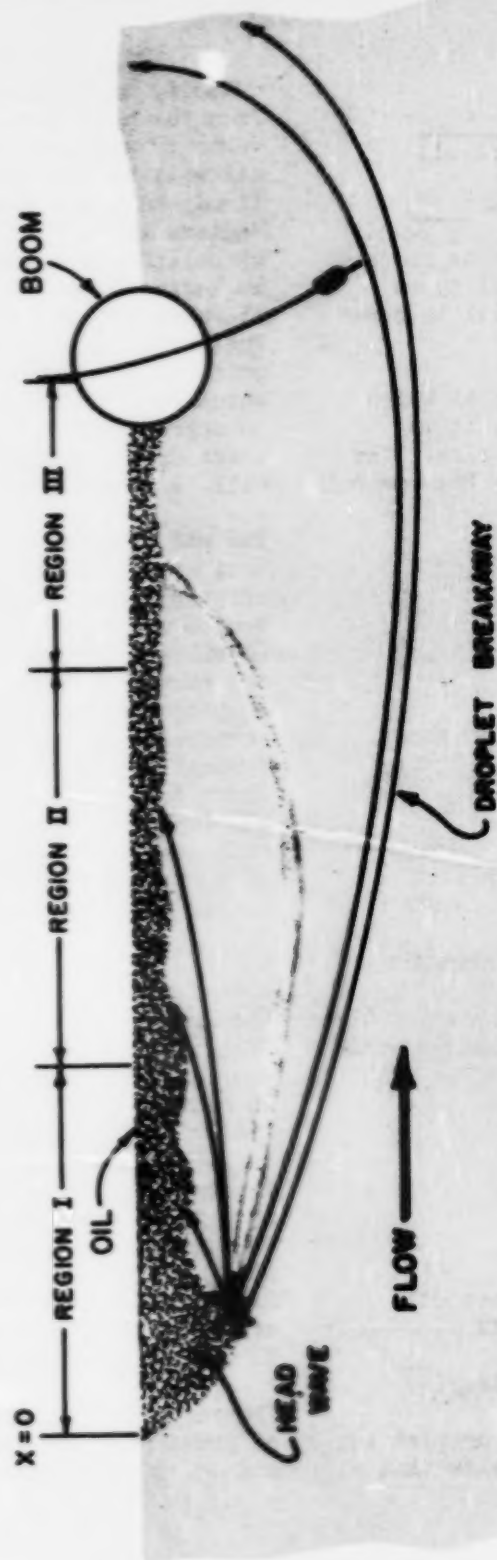
$$h = \frac{u^2}{2g_1 \left(\frac{\rho_o}{\rho_w} - 1 \right)}$$

Where

h - oil film thickness in feet

u - water current in ft/sec

g_1 - acceleration due to gravity
32 ft/sec²



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FIGURE 3

BEHAVIOR OF AN OIL SLICK CONTAINED BEHIND A BOOM

$$\frac{\rho_w}{\rho_o} = \frac{1}{\text{specific gravity of oil}}$$

#2 oil = $\frac{1}{0.8}$ #6 = $\frac{1}{0.99}$

Figure 4 gives the oil thickness for a wide range of currents and oil types. The depth of the head wave will be equal to 2.4 h.

To determine the current (u_c) at which droplet formation will start, it is necessary to predict droplet size. The maximum size possible will be the control.

$$d_{max} = \pi \left[\frac{\sigma E_c}{g, \Delta \rho} \right]^{1/2}$$

Where

d_{max} - max. drop size in feet

σ - oil-water interfacial tension, 30 dynes/cm

E_c - 32.2 ft/sec²

g - acceleration due to gravity 32 ft/sec²

$\Delta \rho$ - water density minus oil density in lbs/ft³

The maximum d which can be achieved with any type of oil is 0.75 inches.

Then

$$u_c = \left[\frac{220 E_c}{\rho_w d} \right]^{1/2}$$

Where

u_c = critical velocity of which oil droplets will be torn off

ρ_w = density of water, 62.4 lbs/ft³

For critical conditions (max. droplet size) u_c will equal 0.62 ft/sec. Below this

velocity no droplets will be released from the head wave. Exceeding this velocity does not necessarily mean that oil will be lost under the barrier. It may be redeposited on the slick in Regions II or III. There will be circulation and drag phenomena working in Region II as well as the generation of waves at the oil-water interface. These will affect the location of the point of reattachment. In Region III which runs from the boom to a point = to approximately 5 times the boom skirt depth, any oil droplet entering will be swept under the boom.

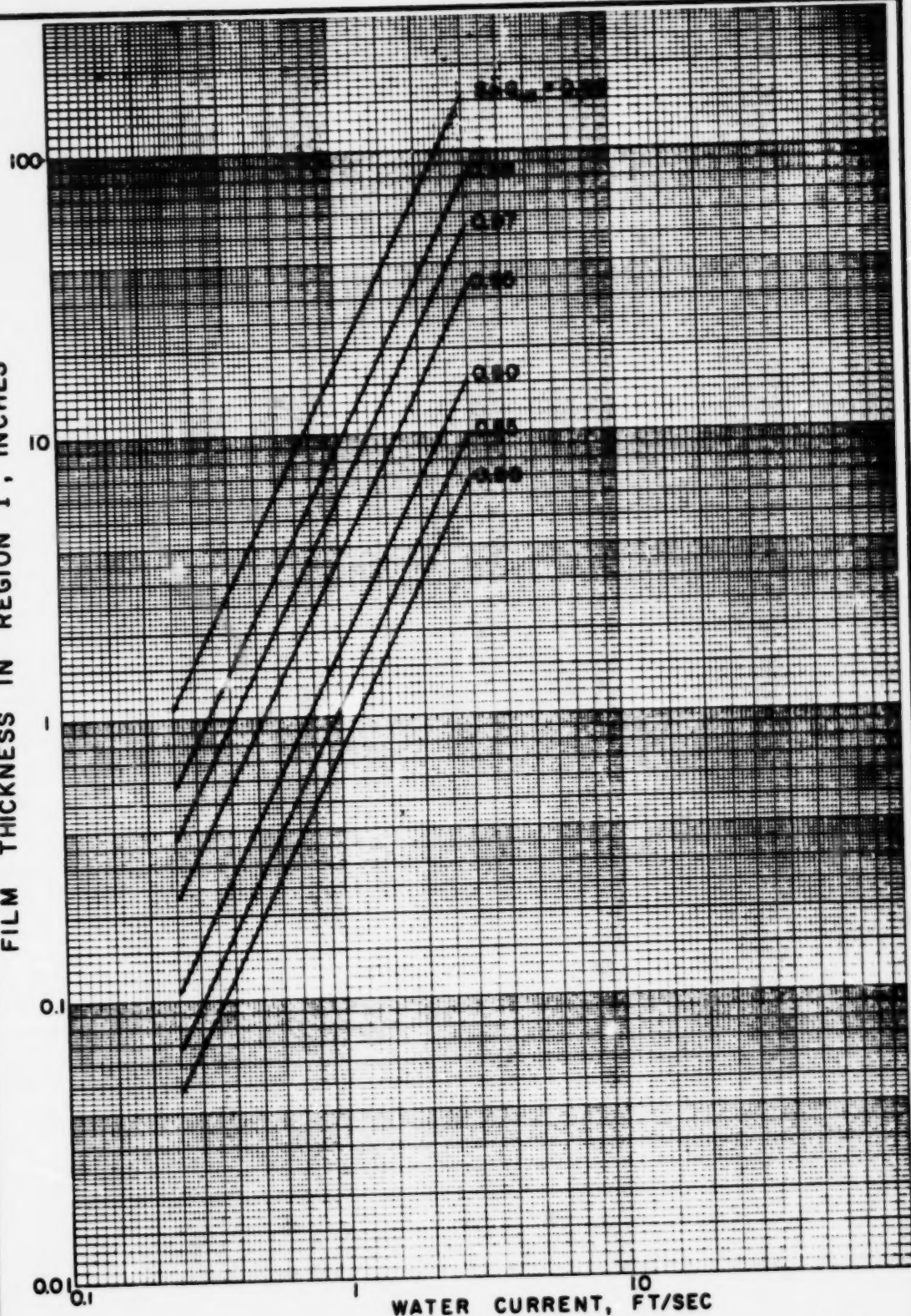
The oil droplet, once released from the head wave, will be affected by the buoyant force, drag force, gravity force, and to a lesser extent, by a negative lift force. These will determine the acceleration of the droplet and the final velocity or terminal rise velocity (V_t) achieved. Typical values for this for No. 2 oil (specific gravity = 0.8) through No. 6 oil (specific gravity = 0.99) are presented in Table 2. If the length of the slick in Regions I and II is longer than

$$2h \frac{u}{V_t}$$

the droplet will reenter the oil layer. If the slick is shorter than this, the droplet will be carried under the barrier to emerge on the other side. The slick length in Regions I and II is going to depend on how the barrier is deployed and the environmental conditions existing when it is deployed. In many cases the maximum possible l will be obvious. In others the use of Figure 4 coupled with an understanding of the principles discussed in Section II will be of assistance.

Figures 5 and 6 provide a graphical means of predicting droplet failure for No. 2 and No. 6 oil respectively. The region

FILM THICKNESS IN REGION I, INCHES



OIL FILM THICKNESS IN REGION I

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FIGURE 4

TABLE 2 - Calculated Terminal Velocities

a. Interfacial Tension = 10 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity						
	.8	.85	.9	.95	.97	.98	.99
0.0010	0.003566	0.002916	0.002195	0.001351	0.000945	0.000711	0.000438
0.0020	0.007133	0.005832	0.004391	0.002703	0.001890	0.001423	0.000876
0.0040	0.014266	0.011664	0.008782	0.005406	0.003781	0.002846	0.001752
0.0065	0.023183	0.018955	0.014271	0.008785	0.006144	0.004626	0.002847
0.0100	0.035668	0.029162	0.021956	0.013516	0.009452	0.007117	0.004381
0.0200	0.071317	0.058317	0.043911	0.027032	0.018906	0.014234	0.008762
0.0400	0.141914	0.116273	0.087688	0.054041	0.037806	0.028467	0.017525
0.0650	0.223815	0.185383	0.141099	0.087549	0.061357	0.046231	0.028473
0.1000	0.307306	0.263190	0.207284	0.132567	0.093750	0.070878	0.043759
0.2000	0.369552	0.339260	0.295863	0.221511	0.170109	0.134129	0.085882
0.4000	0.000000	0.000000	0.000000	0.252218	0.218110	0.190420	0.142903
0.6500	0.000000	0.000000	0.000000	0.000000	0.000000	0.195046	0.161475
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.159074

b. Interfacial Tension = 20 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity						
	.8	.85	.9	.95	.97	.98	.99
0.0010	0.003327	0.002720	0.002048	0.001261	0.000882	0.000664	0.000409
0.0020	0.006655	0.005441	0.004096	0.002522	0.001764	0.001328	0.000817
0.0040	0.013310	0.010883	0.008193	0.005044	0.003527	0.002656	0.001635
0.0065	0.021630	0.017685	0.013315	0.008196	0.005732	0.004316	0.002657
0.0100	0.033278	0.027209	0.020485	0.012610	0.008819	0.006640	0.004087
0.0200	0.066551	0.054416	0.040971	0.025221	0.017639	0.013280	0.008175
0.0400	0.132791	0.108678	0.081887	0.050435	0.035277	0.026561	0.016351
0.0650	0.212642	0.174993	0.132451	0.081841	0.057293	0.043151	0.026569
0.1000	0.306552	0.257795	0.199049	0.124954	0.087860	0.066280	0.040856
0.2000	0.411404	0.371929	0.316105	0.224870	0.166831	0.128913	0.080979
0.4000	0.000000	0.000000	0.342575	0.283933	0.239408	0.203749	0.145302
0.6500	0.000000	0.000000	0.000000	0.000000	0.246480	0.221535	0.177680
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.182599

c. Interfacial Tension = 30 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity						
	.8	.85	.9	.95	.97	.98	.99
0.0010	0.003194	0.002611	0.001966	0.001210	0.000846	0.000637	0.000392
0.0020	0.006389	0.005223	0.003933	0.002421	0.001693	0.001275	0.000785
0.0040	0.012778	0.010447	0.007866	0.004842	0.003386	0.002549	0.001569
0.0065	0.020765	0.016978	0.012782	0.007868	0.005503	0.004143	0.002550
0.0100	0.031948	0.026121	0.019666	0.012106	0.008466	0.006374	0.003924
0.0200	0.063894	0.052242	0.039334	0.024213	0.016934	0.012749	0.007848
0.0400	0.127600	0.104392	0.078636	0.048422	0.033863	0.025500	0.015697
0.0650	0.205385	0.168641	0.127405	0.078617	0.055016	0.041431	0.025508
0.1000	0.302108	0.251981	0.193011	0.120358	0.084467	0.063675	0.039231
0.2000	0.433290	0.387498	0.323712	0.223538	0.163156	0.125044	0.078010
0.4000	0.000000	0.409167	0.370111	0.301460	0.249643	0.208851	0.144561
0.6500	0.000000	0.000000	0.000000	0.000000	0.301918	0.265958	0.185595
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.233599	0.196671

d. Interfacial Tension = 40 Dynes/Cm

Drop Diam. In.	Oil Specific Gravity						
	.8	.85	.9	.95	.97	.98	.99
0.0010	0.003104	0.002538	0.001911	0.001176	0.000823	0.000619	0.000381
0.0020	0.006209	0.005076	0.003822	0.002353	0.001645	0.001239	0.000763
0.0040	0.012419	0.010153	0.007644	0.004706	0.003291	0.002473	0.001525
0.0065	0.020181	0.016500	0.012423	0.007647	0.005348	0.004027	0.002479
0.0100	0.031049	0.025386	0.019113	0.011765	0.008228	0.006195	0.003813
0.0200	0.062098	0.050773	0.038227	0.023532	0.016457	0.012391	0.007627
0.0400	0.124065	0.101483	0.076434	0.047062	0.032916	0.024783	0.015256
0.0650	0.200198	0.164199	0.123937	0.076427	0.053475	0.040263	0.024793
0.1000	0.297655	0.247139	0.188509	0.117163	0.082147	0.061925	0.038132
0.2000	0.446685	0.396188	0.326847	0.221364	0.160068	0.122147	0.075942
0.4000	0.463371	0.432937	0.389363	0.312749	0.255406	0.211015	0.143226
0.6500	0.000000	0.000000	0.000000	0.319628	0.279508	0.246891	0.190127
1.0000	0.000000	0.000000	0.000000	0.000000	0.000000	0.247593	0.206395

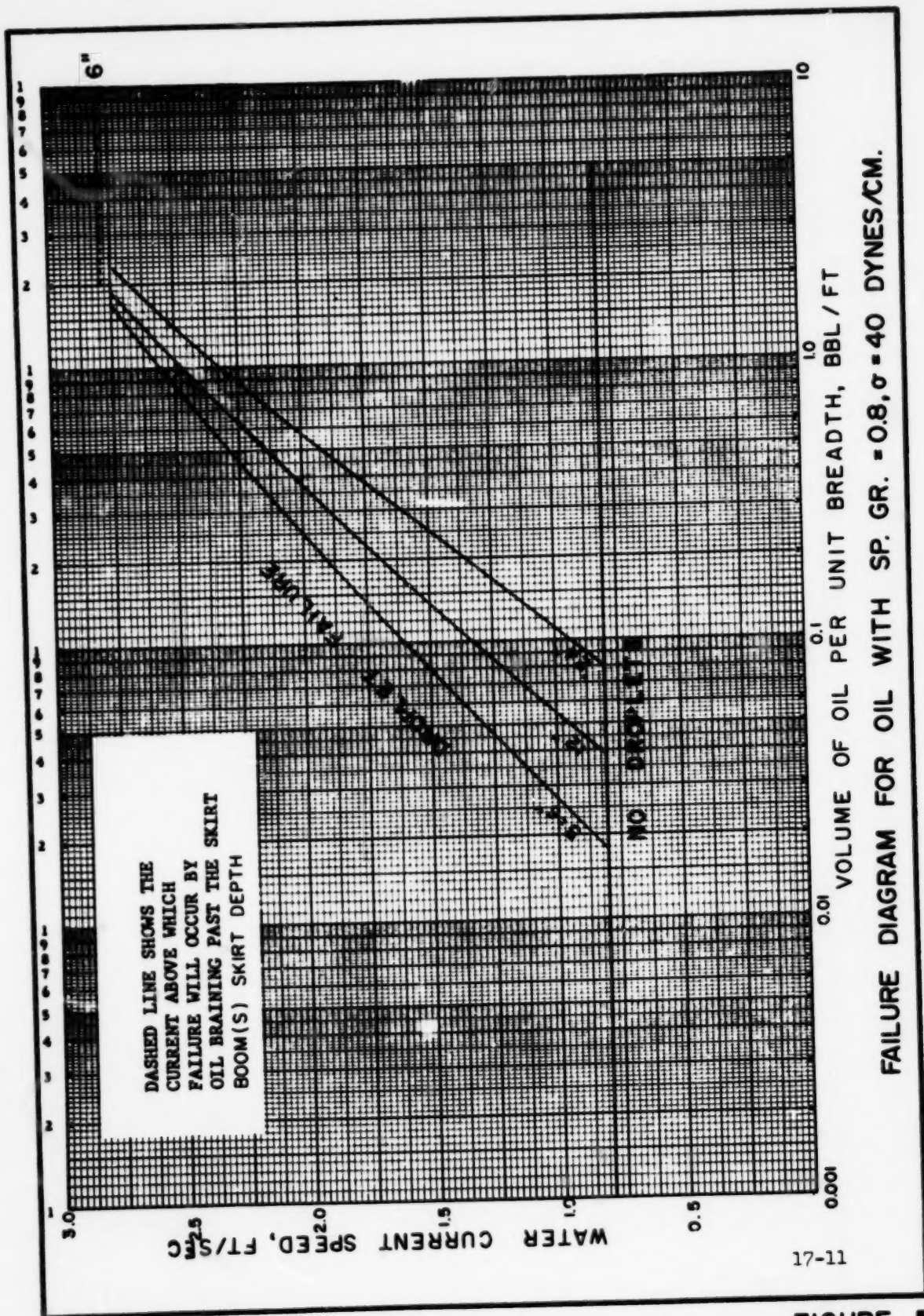


FIGURE 5

FIGURE 6

below the solid horizontal line is completely safe from droplet failure. In the region above the sloping lines, droplet failure is certain. Between the sloping lines and the horizontal line, failure is uncertain. It is in this area that environmental factors, other than those allowed for, may cause problems. The dashed lines on the graph represent failure by "draining." This loss phenomenon occurs when flow conditions exist where oil can plunge under or drain past the boom with the water. Until recently this was felt to be the primary reason for boom failure. This loss can be controlled by changing skirt depth as the loss is essentially independent of the amount of oil spilled. Graphical information for determining the appropriate skirt depth is presented in Figure 7.

The volume of oil per unit breadth of boom may be calculated based on actual field conditions, either existing or predicted. This is the best approach. If this is not possible, the use of the concepts developed or referred to previously have been used to develop Figures 8 and 9. These are for an oil with a specific gravity approximately midway between No. 2 and No. 6. Figure 8 provides information which may be fit into the boom configuration associated with your particular circumstance. Figure 9 provides data for an idealized situation. Additional information may be obtained by consulting the references noted in the Bibliography, particularly No. 9 by Dr. Moye Wicks.

Air barriers are beginning to find some application as protection devices at fixed installations located in fairly quiescent waters. Generally the barrier is made from a pipe, 1 inch I.D. or less, with a series of orifices drilled through the pipe wall 1/16 inch in diameter or less. Air is supplied by either an air compressor or blower.

As an example of capacities required, a 600 cfm compressor is capable of supplying adequate air to 100 feet of 1 inch diameter pipe having 1/16 inch diameter orifices positioned 40 feet below the water surface.

As the air bubbles exit from the pipe and rise to the water surface, they impart momentum to the water. This causes verticle water flow which becomes horizontal at the water surface. The surface current generated retains the oil. Figure 10 illustrates the circulation pattern developed. In calm waters the maximum surface current (v_{max}) created is related to the volume flow rate of air per unit length of pipe.

$$v_{max} = k(gQ)$$

Where

v_{max} - maximum generated surface current ft/sec

k - a constant

g - acceleration due to gravity
32 ft/sec²

Q - volume flow rate/unit length of manifold

The surface current reaches a maximum at a distance from the center line of the barrier varying between d and $d/2$ where d is the distance between the undisturbed water surface and the location of the manifold (see Figure 10). It then decreases approximately proportional to $\frac{1}{x}$ where x = the horizontal distance from the manifold. The effective depth of the surface current (b) is $\frac{1}{2}$ at $x = 1$ and increases linearly for a larger x .

Water currents will cause a distortion in the plume (see Figure 11). This

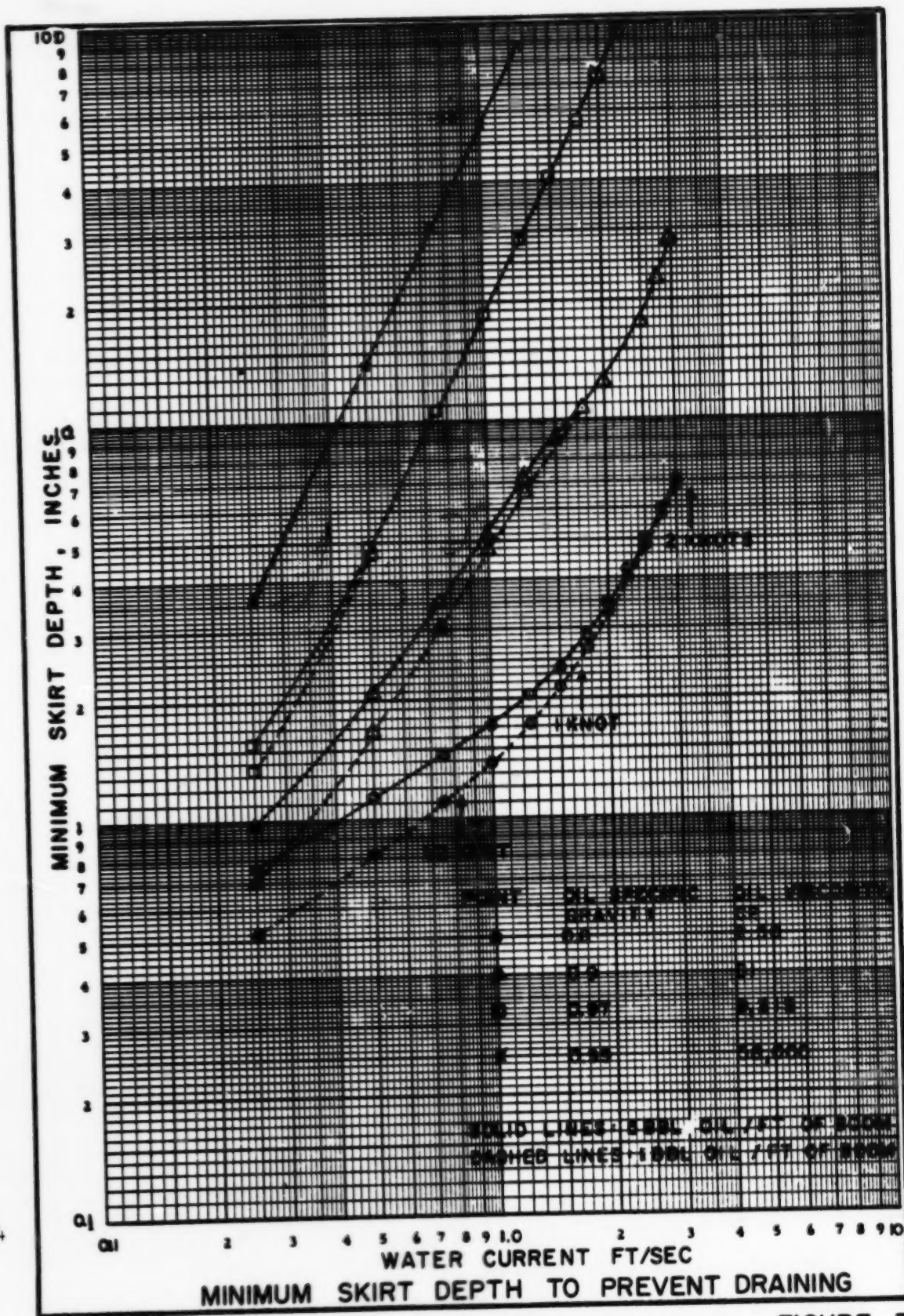


FIGURE 7

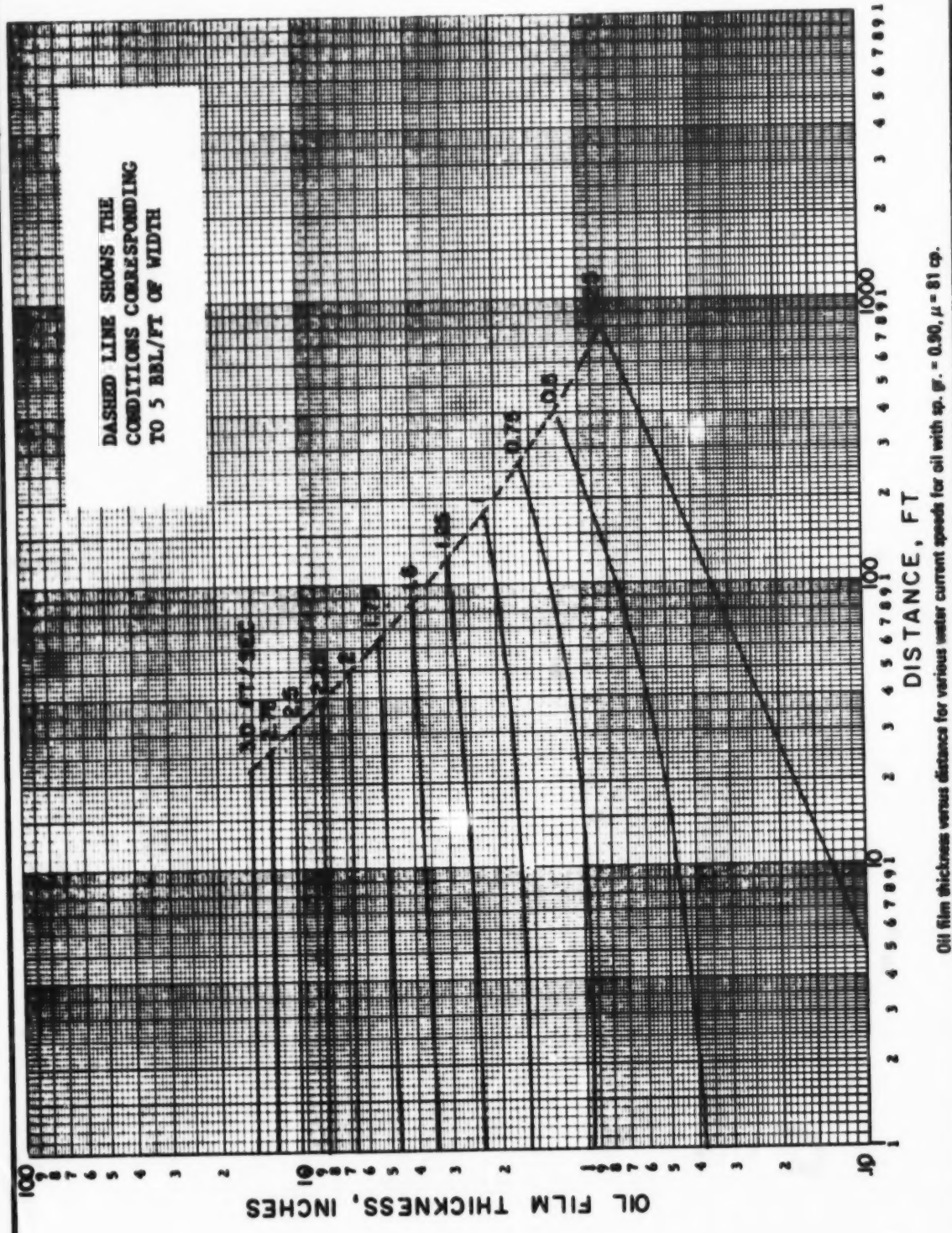


FIGURE 8

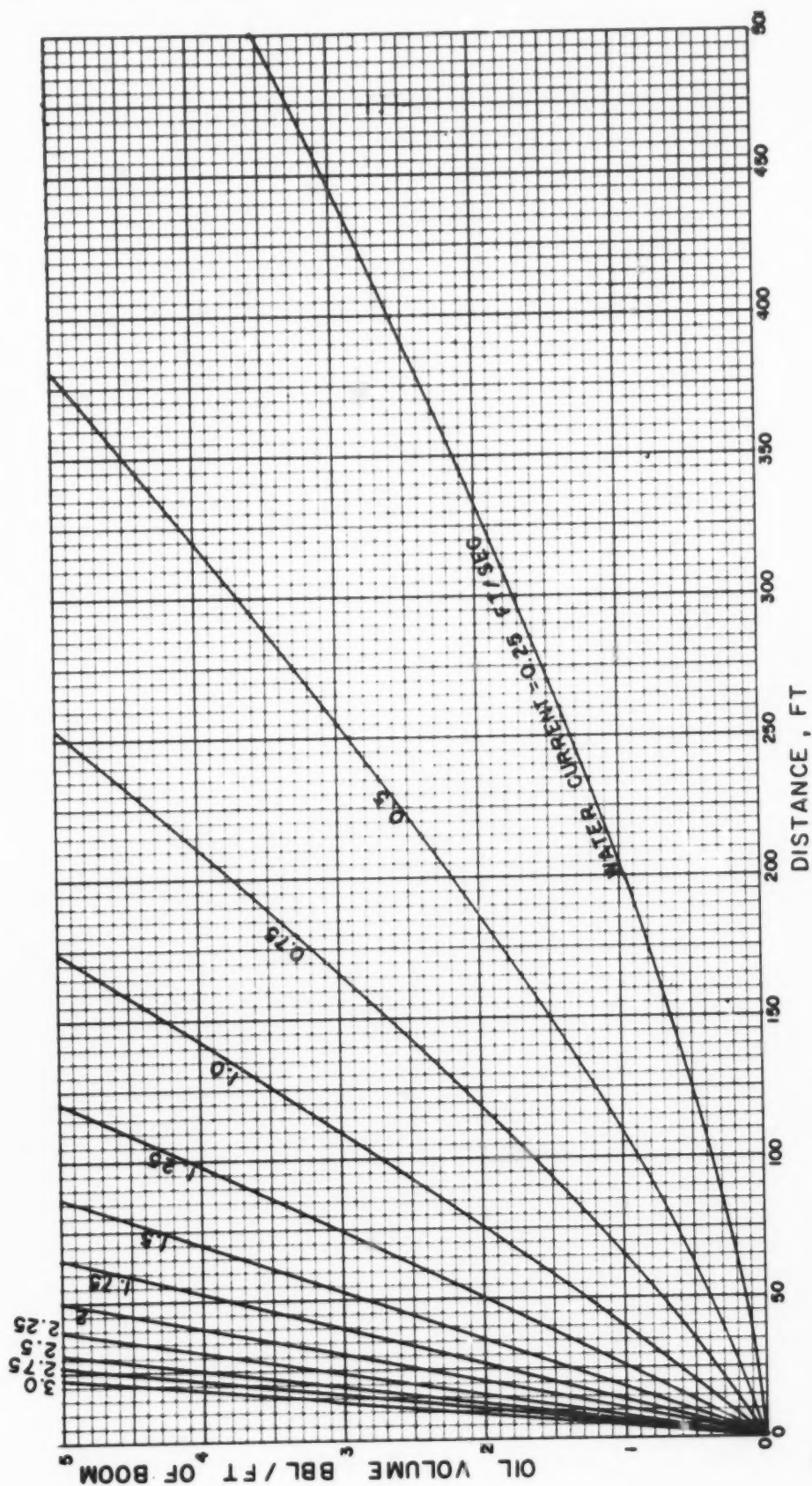
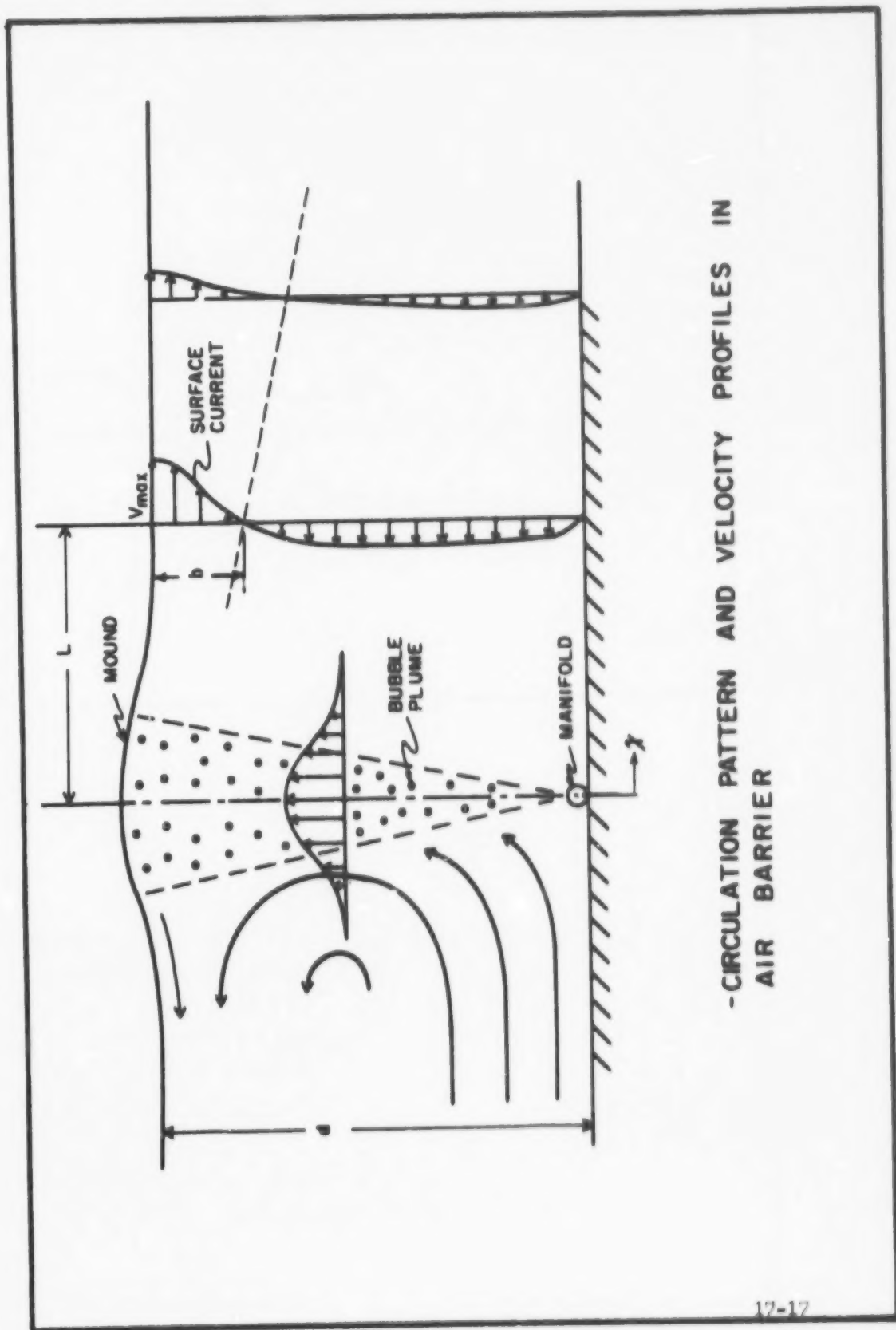
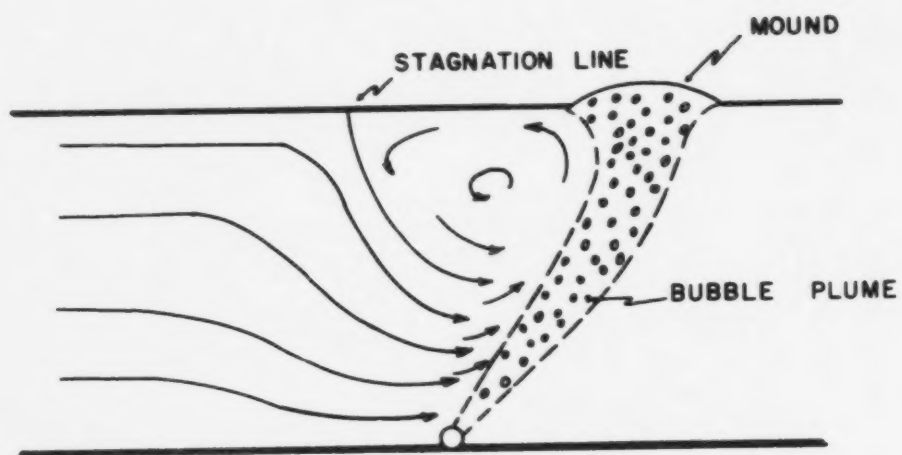


FIGURE 9

Cumulative oil film volume per unit width at various distances and water velocities for oil with $\text{sp. gr.} = 0.90$, $\mu = 81$ cp.



-CIRCULATION PATTERN AND VELOCITY PROFILES IN
AIR BARRIER



- CIRCULATION PATTERN UPSTREAM OF
AN AIR BARRIER IN A CURRENT

distortion creates a flow pattern which will allow some of the oil to disperse through the bubble screen. The greater the current, the more severe will be the problem. As with a mechanical barrier, oil drops are lost from the bottom of the slick; in this case, because of the turbulent pattern produced.

The information presented is intended to provide the oil pollution control officer with a basis for making recommendations and with the hope that it will provide him with an understanding of the phenomena with which he is dealing. It is expected that his experiences in the field will modify these concepts so that they best serve the needs of his environmental area.

IV BOOM DESIGNS

The information having now been presented concerning the factors which should influence boom design and the mechanisms by which they are most likely to fail, what types of barriers are commercially available? What capabilities should the boom have in addition to that most important one of oil retention?

One of the more important is transportability. Cleanup equipment, in general, should be designed for easy transportation from some centralized storage point to the site of a pollution incident. A modular system designed for air transport would be best. Once the equipment is on site, ease of deployment is essential. Regrettably, spills are not in the habit of occurring in ideal weather conditions. The equipment should be designed to provide maximum compatibility with the type of watercraft that are likely to be used in its deployment. In particular, weight handling, towing, and equipment assembly requirements, should be selected with the capabilities of available vessels in mind. The barrier system design should also be as

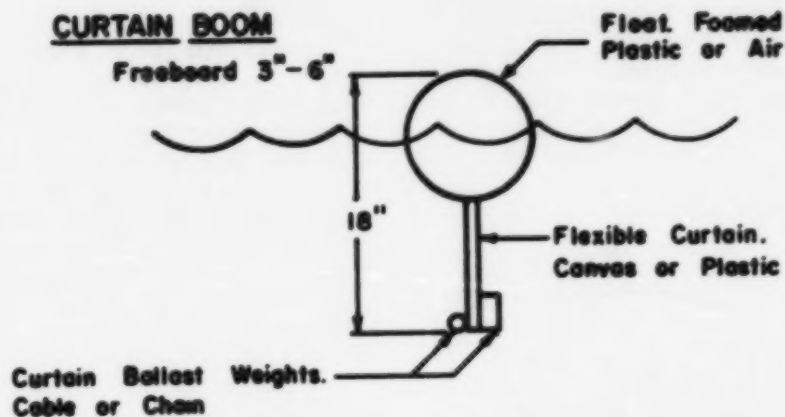
compatible as possible with the other cleanup equipment available. Such a simple thing as non-compatible connecting hitches can destroy a well laid-out spill control program. Last of the major points but by no means least, the containment system should be mutually supporting to the recovery system. Containing an oil spill without matching provisions for optimum physical removal is winning less than half the battle. Wherever possible, components within the barrier system should be readily adaptable for use with the oil removal system. Oil retained and not removed will end up being oil lost to the environment.

The types of equipment available may be broadly categorized into three mechanical-type designs and pneumatic barriers. The mechanical barriers are:

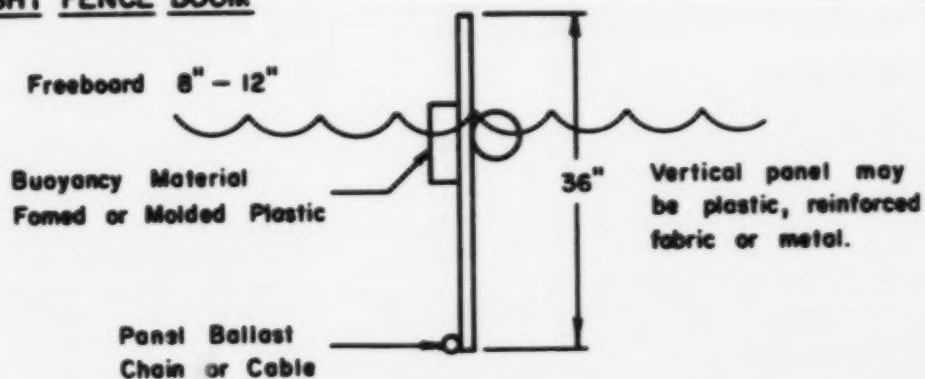
- 1 "Curtain booms" which consist of a surface float acting as a barrier above the surface and a subsurface curtain suspended from it. The curtain is flexible along the vertical axis. It may or may not be stabilized by weights to provide greater resistance to distortion by subsurface currents and have a chain or welded wire rope to transfer stress along the barrier.
- 2&3 Light and heavy "Fence booms" have a vertical fence or panel extending both above and below the surface of the water to provide freeboard to counteract wave carryover and draft below the water surface. The flotation assembly is generally bonded to the fence material. The lower edge of the panel is frequently stabilized and strengthened by a cable or chain. The distinction between light and heavy is generally one of size of components and weight.

The general characteristics of these

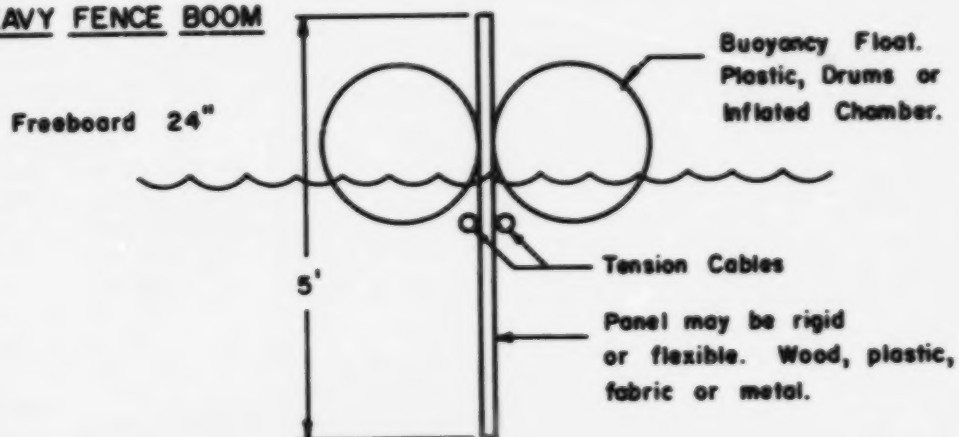
CURTAIN BOOM



LIGHT FENCE BOOM



HEAVY FENCE BOOM



TYPICAL BOOM DESIGNS

SUMMARY TABLE 1

COMMERCIAL FLOATING BOOMS

<u>Boom</u>	<u>Stage of Development</u>	<u>Cost \$/Ft.</u>	<u>Manufacturer</u>
1. Abribat Boom	Under Patent	Unknown	Address Unknown France
2. Aqua Fence	Under Development	Unknown	Versatech Corporation Nesconset, Long Island New York
3. Boom Kit	In Production	Unknown	Roberts Plastics Ltd. England
4. Bristol Aircraft Company Boom	In Production	Unknown	Bristol Aircraft Company England
5. British Petroleum Company Boom	Under Patent	Unknown	British Petroleum Company Pinsburg Circus London, E. C. 2, England
6. California Oil Company Boom	In Production	\$2.45	California Oil Company Perth Amboy, New Jersey 07501
7. Elo-Boom	In Production	\$2.20	Helly J. Hansen A/S Moss, Norway
8. English China Clay Company Boom	In Production	Unknown	English China Clay Company England

Boom	Stage of Development	Cost \$/Ft.	Manufacturer
9. Flexy Oil Boom	In Production	Unknown	Smith-Anderson Company, Ltd. 3181 St. James Street West Montreal, Quebec
10. Flo-Fence	In Production	Unknown	Logan Diving & Salvage Co. 530 Goodwin Street Jacksonville, Florida 32204
11. Galvaing Floating Booms	In Production	\$16.20-\$22.40	Gamlen Maintre & Cie 92 Clichy, 2, Rue Huntziger, France
12. Gates Boom Hose	In Production	\$50.00	Gates Rubber Company 6285 East Randolph Street Los Angeles, California 90022
13. Headrick Boom	Under Development	Expected Price \$25-\$35	Headrick Industries, Inc. 4900 Crown Avenue La Canada, California 91011
14. Jaton Boom	In Production	Unknown	Centri Spray Corporation 39001 Schoolcraft Road Livonia, Michigan 48150
15. Johns-Manville Spillguard Booms	In Production	\$7.50-\$20.00	Johns-Manville Company 22 East 40th Street New York, New York 10016
16. Kain Filtration Booms	In Production	\$18.00-\$23.00	Bennett International Service 302 A-5645 Topanga Canyon Boulevard Woodland Hills, California 91364

Boom	Stage of Development	Cost \$/Ft.	Manufacturer
17. Marsan Inflatable Oil Barrier	In Production	\$5.95 - \$6.95	Marsan Corporation Box 83, Route 1 Elgin, Illinois 60120
18. MP Boom	In Production	\$9.75	Metropolitan Petroleum Company, Inc. 25 Caven Point Road Jersey City, New Jersey 07305
19. Muehleisen Boom	In Production	Submitted Upon Request	Muehleisen Manufacturing Co. 1100 North Johnson Avenue El Cajon, California 92020
20. Oscarseal - Hover Platforms	Patent Pending	Submitted Upon Request	The Rath Company P.O. Box 226 La Jolla, California 92037
21. Oscarseal - Steel Boom	Patent Pending	\$40 - \$50	Morrison-Knudsen Company, Inc. Box 7808 Boise, Idaho 83707
22. Red Eel	In Production	\$2.60	Trelleborg Rubber Company, Inc. P.O. Box 178 225 Main Street New Rochelle, New York 10802
23. Retainer Seawall	Patent Pending	\$20.00 light duty \$58.60 heavy duty	Environmental Pollution Systems 209 Profit Drive Victoria, Texas 77901

Boom	Stage of Development	Cost \$/Ft.	Manufacturer
24. Sea Curtain	In Production	\$ 2 - \$ 4 light duty \$10 - \$15 heavy duty	Kepner Plastics Fabricators, Inc. 4221 Spencer Street Torrance, California 90503
25. Sea Fence	Experimental	Unknown	Aluminum Company of America 4-63 48th Avenue Long Island City, N.Y. 11101
26. Sealdboom	In Production	\$12.00	Uniroyal, Inc. 10 Eagle Street Providence, Rhode Island 02901
27. Sea Skirt	Developmental	Unknown	Core Laboratories, Inc. Box 10185 Dallas, Texas 75201
28. 6-12 Boom	In Production	\$ 9.75	Worthington Corporation Pioneer Products Division P.O. Box 211 Livingston, New Jersey 07039
29. Slickbar Oil Boom	In Production	\$3.85-\$ 6.80, 4" \$5.25-\$12.25, 6"	Neirad Industries Saugatuck Station Westport, Connecticut 06880
30. SOS Booms	In Production	\$5.50-\$16.50	Surface Separator Systems 103 Mellor Avenue Baltimore, Maryland 21228

<u>Boom</u>	<u>Stage of Development</u>	<u>Cost \$/Ft.</u>	<u>Manufacturer</u>
31. Transatlantic Plastics Boom	Unknown	Unknown	Transatlantic Plastics Ltd. England
32. T-T Boom	In Production	\$6.77-\$8.08	East Coast Service, Inc. 343 Washington Street Braintree, Massachusetts 02184
33. Warne Booms	In Production	\$15.00-\$36.00	Surface Separator Systems 103 Mellor Avenue Baltimore, Maryland 21228
34. Water Pollution Controls Boom	Patent Pending	Unknown	Water Pollution Controls, Inc. 2035 Lemoine Avenue Fort Lee, New Jersey 07024

designs are shown in Figure 12.

There are over 50 different commercially-available booms that would fit into these three categories available at the present time. A partial listing is presented in Table 1. More detailed information for one example of each type follows. For additional information, it is suggested that you consult Bibliography reference No. 6.

Curtain Boom - Slickbar

The Slickbar boom manufactured by Slickbar, Inc., Westport, Connecticut, is probably the most popular and most commonly encountered of the curtain booms presently available. All of their present designs consist of a cylindrical-closed cell, foamed-plastic float with a flexible plastic curtain extending approximately half-way into the float. The curtain is secured to the float by a series of stainless steel straps which are riveted to the fin at appropriate intervals depending on float size. Lead ballast is riveted to the bottom of the flexible curtain. The amount and spacing depends upon the environmental conditions expected at the use site. A $\frac{1}{4}$ -inch stainless steel cable runs the length of each boom section immediately below the plastic float and inside of the stainless steel strapping (see Figure 13).

The booms are available in 4- and 6-inch float diameters with curtain (fin) depths available from 6 to 24 inches. Standard sections are available in 4- and 9-foot float lengths with 6 inches of plastic fin extending beyond each end terminating with stainless steel connector plates. This extends the effective length of each boom to 5 and 10 feet respectively. The sections are connected to provide a continuous barrier.

Prices for the 6-inch diameter float boom in 10-foot lengths complete with ballast weights, ranging from 0.9 to 3.6 pounds per linear foot and having fin depths available from 6 to 24 inches, range from \$6.40 to \$9.85 per linear foot. These booms are intended for use in relatively quiescent waters of the type found in lakes and protected in harbor areas. A larger and heavier boom with a 12-inch float and 24-inch skirt is presently under development by Slickbar for use in estuarine areas where rougher waters are encountered. This will cost approximately \$12.25 per linear foot.

Light Fence Boom - "T-T" Boom

The "T-T" boom was developed in Norway and is presently being manufactured in the United States and marketed by Coastal Services, Inc., a Division of Ocean World. This boom is becoming increasingly popular for use in calm and moderate water conditions. It consists of a vertical section, either 15 or 36 inches deep made of 300 pound per inch tensile strength PVC plastic-coated nylon fabric. Aluminum rods are sewn into the nylon fabric running vertically from top to bottom at either 2- or 3-foot 4-inch spacing. Lead weights are permanently fixed to the fabric at appropriate intervals on the lower edge of the boom generally beside the vertical aluminum rods. Increased ballast may be provided by means of a chain or wire rope threaded through eyelets on the bottom of the curtain. Plastic floats, either rigid-sealed polystyrene type or a closed cell foamed plastic, are attached to the barrier by means of a sash chain with a toggle bar (cotter pin type arrangement). These are generally spaced to fall along the vertical aluminum rods, and are positioned such that two-thirds the height of the barrier is below the

water and one-third above. The boom is manufactured in standard lengths of 50 meters (164 feet) which weigh approximately 220 pounds per standard length. One hundred foot standard lengths are also available. A terylene rope running through brass rings fixed on both top and bottom edges of the curtain which made it possible to contract the boom in an accordion-like fashion to reduce the encircled area of an oil spill, is being discontinued due to fouling problems in use. Boom sections are connected by means of a 2-foot overlap of nylon with appropriate hook and tie lines (see Figure 14).

One of the advantages of the barrier is its lightweight and removable, easily attachable floats. Fifty meters of barrier may be stored in a 3 by 4 foot area and launched by one man pulling and attaching floats in a short period of time. When the "T-T" boom is towed in the water to a site for use or towed in a sweeping action to compact an oil slick, the ends of the boom may be equipped with aluminum paravanes for greatest stability and ease in handling. A pair of paravanes weighs approximately 220 pounds.

The prices for the 3-foot barrier, having vertical stiffeners spaced 2 feet on centers with the polystyrene floats, was \$9.50 per foot. A pair of aluminum paravanes are \$724 per pair and special magnet clamps designed to attach the boom to vessels and sheet pilings are \$376 per pair.

Heavy Fence Boom - "Headrick Boom"

This boom is manufactured by Headrick Industries, Inc., LaCanada, California. It is made up from a series of air inflatable cylinders in varying configurations designed for different sea conditions. The boom cylinders are constructed from high-strength PVC

impregnated into a high-strength nylon fabric. A series of air-filled flotation cylinders are positioned above a water-filled submersible cylinder. The water-filled cylinder provides ballast and stability to the total boom assembly. The tubes, as few as two or as many as four, are interconnected continuously by a PVC-coated nylon fabric membrane. A steel cable is permanently enclosed in a loop of the fabric attached to and suspended below the water-filled ballast tube (see Figure 15).

The air tubes are segmented every 50 feet and the water tube every 20 feet so as to provide boom integrity when damaged. The boom is kept stored in a deflated unfilled condition. When needed, it is either unrolled or unfolded and each chamber separately filled with air and water from a surface vessel. The inflatable tubes are reported to retain their air supply for several weeks. If the application situation requires that the boom remain in the water for long periods of time without surveillance, the air tubes may be filled with polyethylene beads, expanded styrofoam or similar materials. Once inserted, however, it is not practical to remove these materials. They also detract one of the barriers more desirable characteristics, its flexibility.

A boom made up of 3 ten-inch diameter air tubes and a 10-inch water tube, weighs approximately 1.8 pounds per foot deflated. Booms will be available in 10, 13, 16 and 22 inch tube sizes. The 22-inch tube unit will weigh 3.6 pounds per foot. The standard length is 1,000 feet which is composed of four 250-foot sections complete with the necessary coupling hardware. These cost \$25,000 to \$35,000 per standard length.

In addition to the above, some special multi-purpose mechanical booms are

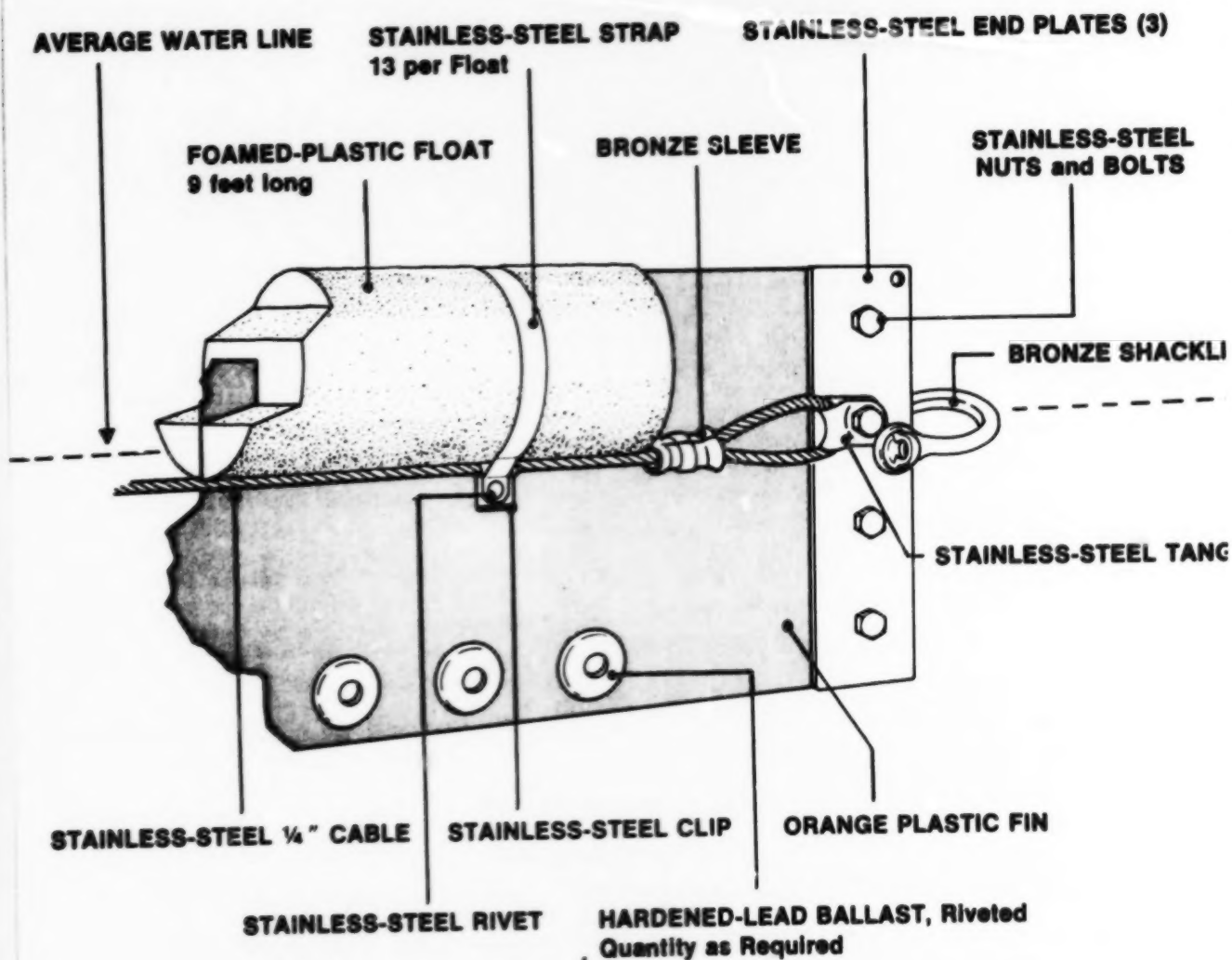


Fig. 13 SLICKBAR Boom

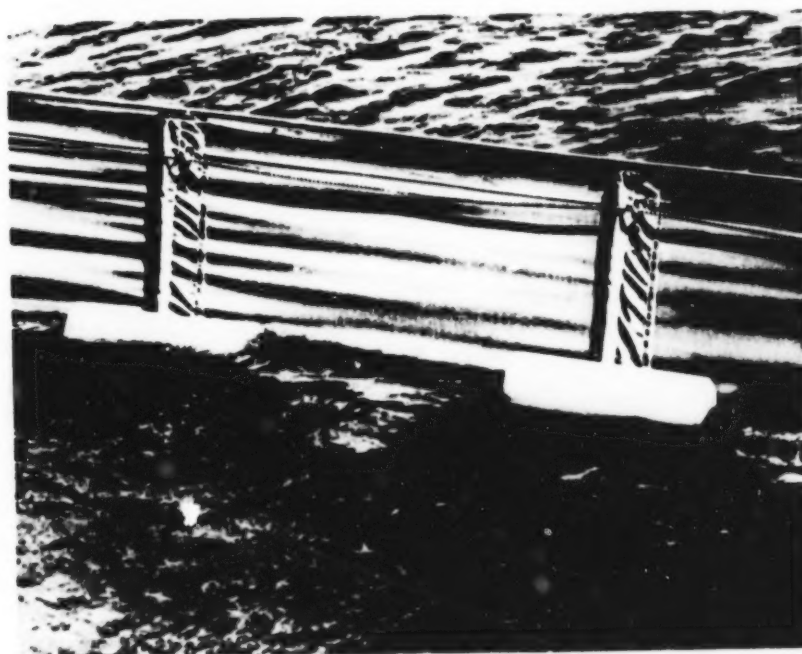
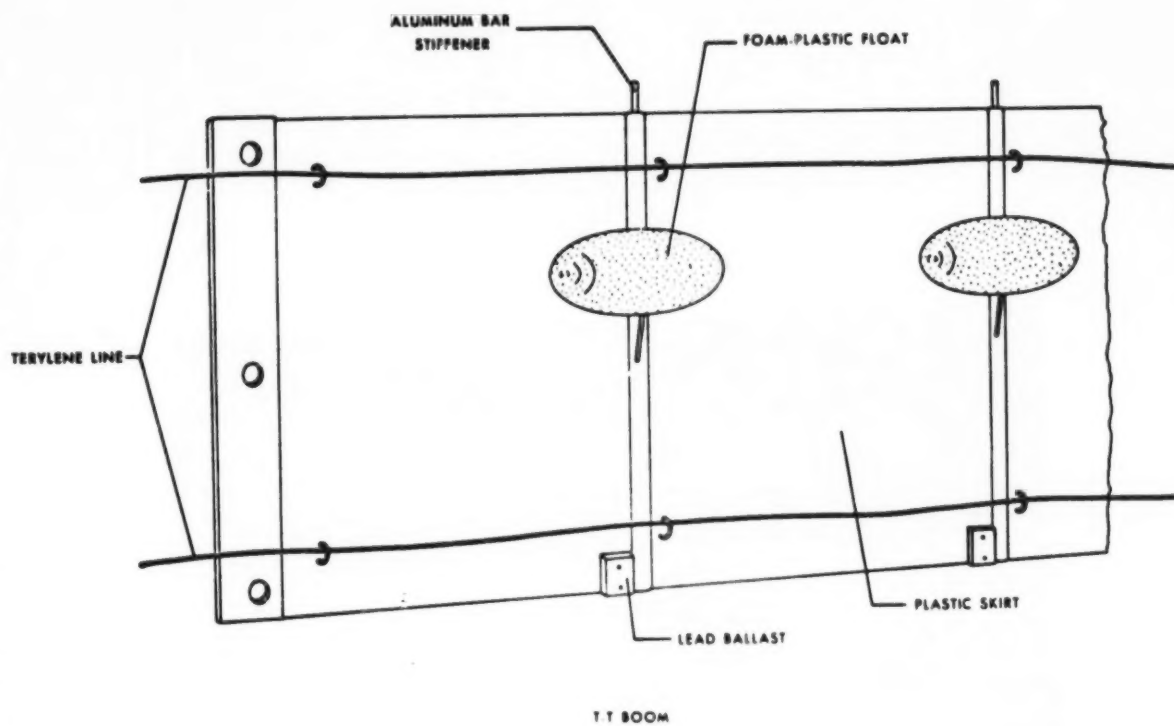


Figure 14
T-T BOOM

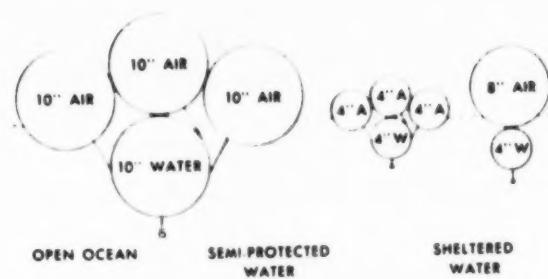


Figure 15
HEADRICK BOOM

SUMMARY TABLE 2

MULTIPURPOSE BOOMS

<u>Boom</u>	<u>Stage of Development</u>	<u>Cost \$/Ft.</u>	<u>Manufacturer</u>
1. ICI Oil Absorbing Boom	In Production	\$6.75 - 7.45	ICI Fibres Ltd. Harrogate Yorashire, England
2. Roscoff Heavy and Light- Weight Booms	Used at Torrey Canyon Spill	Unknown	Marise Biological Laboratory Roscoff North Brittany, France
3. Sea Serpent	Under Development	Unknown	Johns-Manville Co. 22 East 40th Street New York, New York 10016
4. Skimmer Boom	Patent Pending	Unknown	E. P. Hall FARCA Washington, D.C. 20242

SUMMARY TABLE 3
IMPROVISED BOOMS

<u>Type of Boom</u>	<u>Location Where it was Used</u>
1. Cork-Filled Boom	Norfolk, Virginia
2. Cork-Float Boom	Port Hueneme, California
3. Fire Hose Boom	Quiescent Waters
4. Puerto Rican Boom	<u>Ocean Eagle Oil Spill</u>
5. Rubber Bladder Boom	Helford River, Great Britain
6. Rubber Tire Boom	<u>Torrey Canyon Oil Spill</u>
7. Steel Pipe Boom	Philadelphia, Pennsylvania
8. U. S. Navy Boom	Long Beach, California: Chevron Spill, 1970
9. Wooden Float Boom	Pearl Harbor, Hawaii
10. Wooden Timber Boom	Quiescent Waters
11. Wooden V-Boom	Peros Gyiroc, France

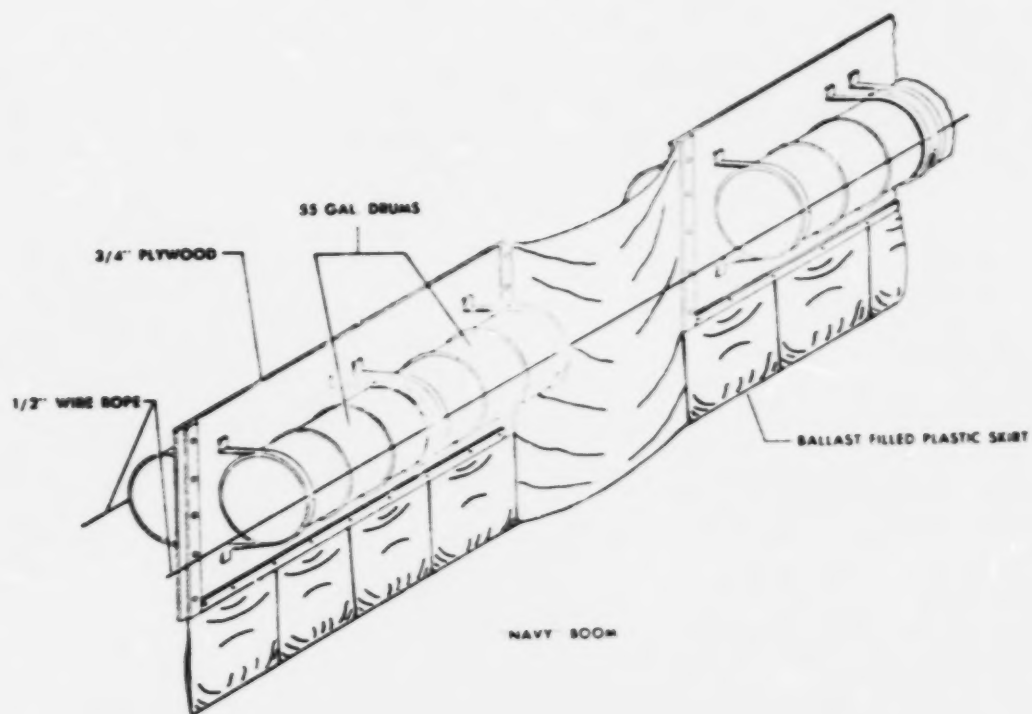


Figure 16
NAVY BOOM



presently available. Some are designed to provide ab/adsorbing capability, others integral skimming capability along with their oil-retaining function. A partial listing of these is presented in Table 2.

In many cases, a commercial boom is not available when an oil pollution incident occurs and maximum use of available materials must be made to provide at least temporary containment or diversion capability until better equipment can be brought to the site. A partial listing of homemade barrier types is presented in Table 3. One of the more famous of these is the Navy boom shown in Figure 16.

The use of air curtains for oil slick containment was discussed in Section 3 and an example of one type presented. Submersible Systems, Inc., Palm Beach, Florida, manufactures an air barrier system. In general it is designed for the environmental conditions existing at the use location. One unit placed in operation consisted of 20-foot lengths of 1-inch inside diameter aluminum pipe with 1/16 inch diameter holes spaced every 6 inches along its length. The sections were connected with a semi-flexible compression-type coupling. Air was supplied by a 600 cfm compressor operating at 45 psi. The cost for this type of barrier will vary with the site location.

V EXAMPLE OF USE

The following is a narrative presentation illustrating one possible use of oil booms for the control of an oil spill. It does not specifically represent any singular pollution incident but rather reflects techniques which met with at least some degree of success in actual incidents.

A vessel with a cargo of crude oil struck a submerged object in the

navigation channel approximately 4 miles from shore. The forward center and starboard tanks were holed and approximately 1,000 barrels of a fairly heavy crude oil lost before leakage was controlled. At present the sea is calm and the current immediately off of the channel where the oil was lost is approximately 2 knots. The wind is blowing steadily from the south at about 9 knots and will move the oil slick northerly toward a beach area. Making use of information previously presented, it is determined that oil will begin reaching the beach area in about 12 hours. Considering the time involved, it is likely that at least part of the slick will reach the shoreface area and that some procedures will have to be implemented for its protection. You want to get equipment out to the site of the slick as soon as possible to remove as much as possible before it does reach the beach area.

You have two skimmers available having a combined capacity of about 600 gallons per minute (water-oil). Work boats, fishing boats, various types of absorbers, and 1,500 feet of light fence boom, and 1,000 feet of pneumatic barrier. Making use of the information previously presented in Sections 2 and 3, you determine that your best defense barrier will not be capable of holding the oil offshore in a fixed position while you pump it off of the water. You have also determined, based on the relative wind velocity, current situation, and the type of spread to be expected from this particular grade of oil, that without some type of containment, you will have a thin film of oil coming ashore within 12 to 14 hours. (See Figure A)

The following is one approach that might be followed. Put your larger skimmer on a work boat along with 900 feet of the fence type barrier and

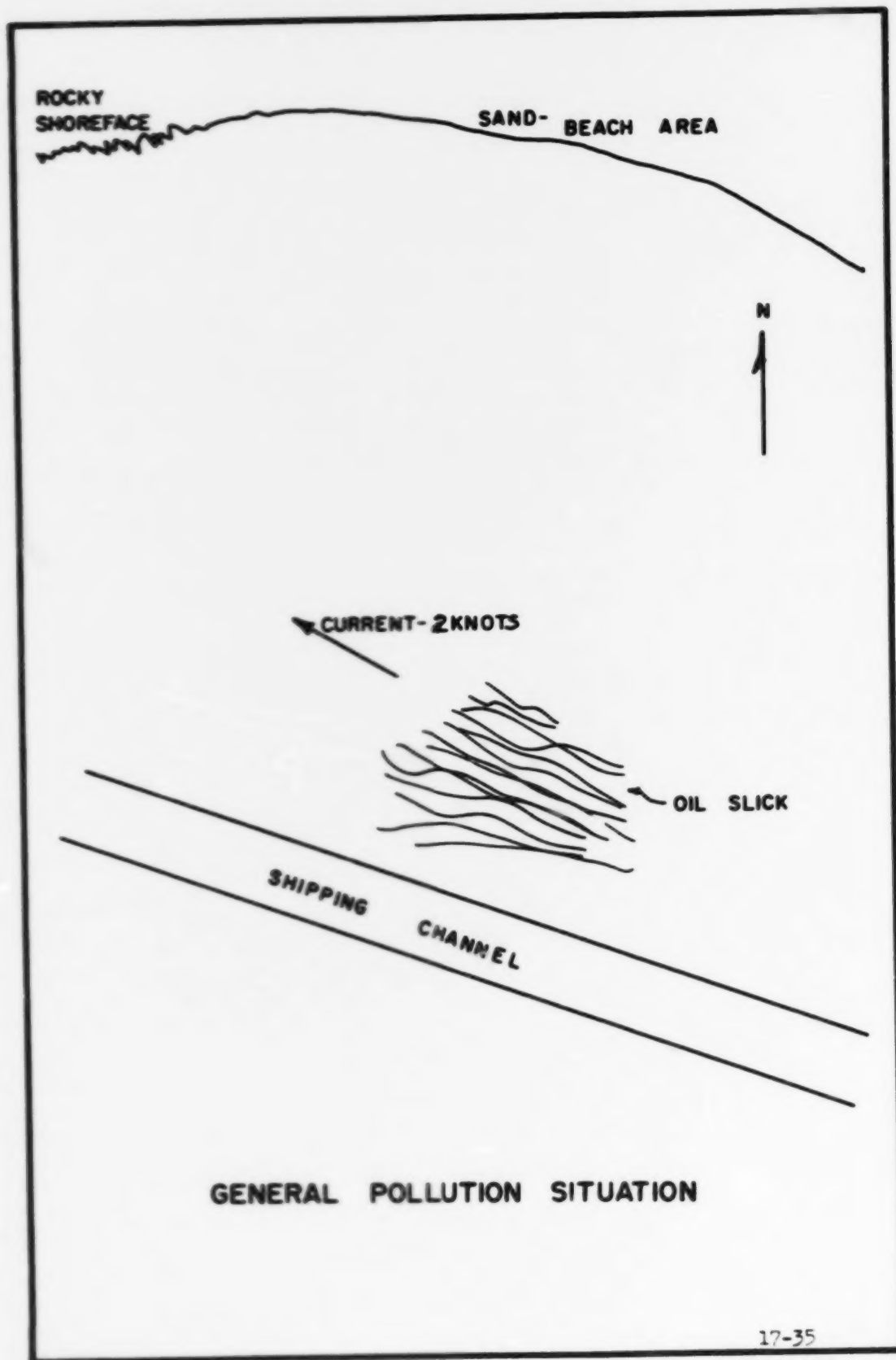


FIGURE A

proceed out to the site of the slick. Set up your equipment as shown in Figure B. The skimmer should be positioned so as to work in the pool of oil collected by the barrier. Note that one end of the boom is held close alongside the work boat and skimmer with a small boat out at the other end. The oil will collect along the wind side of the boom and then be diverted along the boom to the skimmer. The skimmer should be operated at capacity with the oil-water mix being discharged to some type of storage facility for oil-water separation. Note that -

- 1 There must be an oil tight connection between the skimming unit and the boom at a and the boom and the work boat at b.
- 2 The position of the upwind end of the boom and the work boat itself must be changed quickly as the wind shifts. The flow of the slick must continue into the area between the boom and the pump boat.
- 3 The angle between the wind direction and the boom should not be greater than 20 degrees. With more angle the boom will tend to develop a belly in its shape and oil will be lost under the boom.
- 4 The work boat and the boat holding the leading edge of your boom are drifting at a speed which you have previously determined will not allow oil to be lost under the barrier. This speed will, of course, be adjusted based on on-site conditions.

No comments will be made about the type of skimmer, oil-water separation system, or storage system. These are obviously

a very important concern and will control the speed at which the recovery system will move with the slick to prevent loss. Information concerning these is presented in other parts of the training manual.

You now have two other problems to contend with -

- 1 It is obvious from your calculations that it will not be possible to remove all of the oil from the water surface before it gets into the beach area.
- 2 The slick is not remaining as one integral mass and portions of it are breaking away and being left behind in the bay.

Next, consider handling those portions of the slick being left behind in the bay. Two small fishing boats and a contractor's work boat having flat deck space in the bow, have been contracted for and the remaining fence boom and the small skimmer mounted on them. These can be arranged as shown in Figure C. The bow string tension line attached to No. 2 boat reduces the sharp bend that would otherwise exist in the boom and eliminates turbulence and oil loss at the point where the boom would ordinarily bend when it joins the work barge as with No. 1 boat. With the boom system so deployed, this work group begins chasing those slicks left behind and using the small skimmer, pumps them to appropriate storage. The operating speed of this group is controlled by the structural strength of the boom in question which has been considerably increased with the bow string arrangement, and the thickness of oil being recovered at any one time. Remember that the wind should be used to your advantage whenever possible to assist in diverting the oil down the funnel. Note that radio communication among

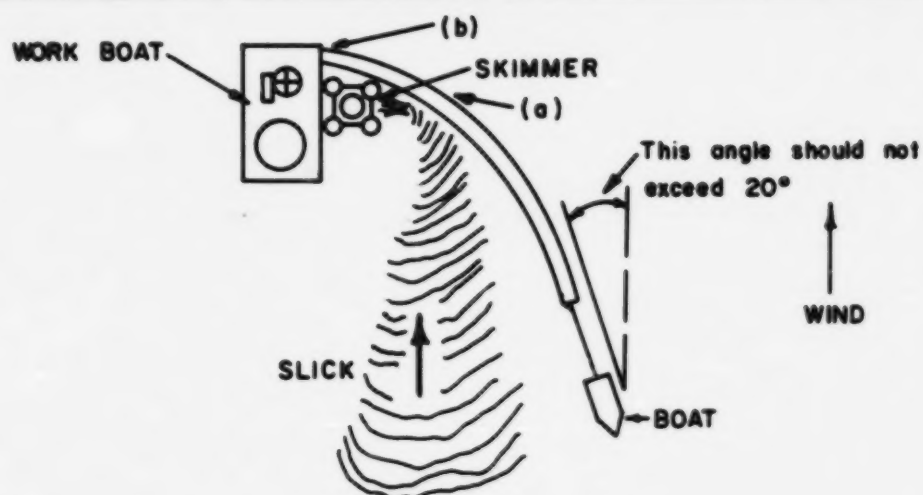


FIGURE B. MAIN SLICK RECOVERY

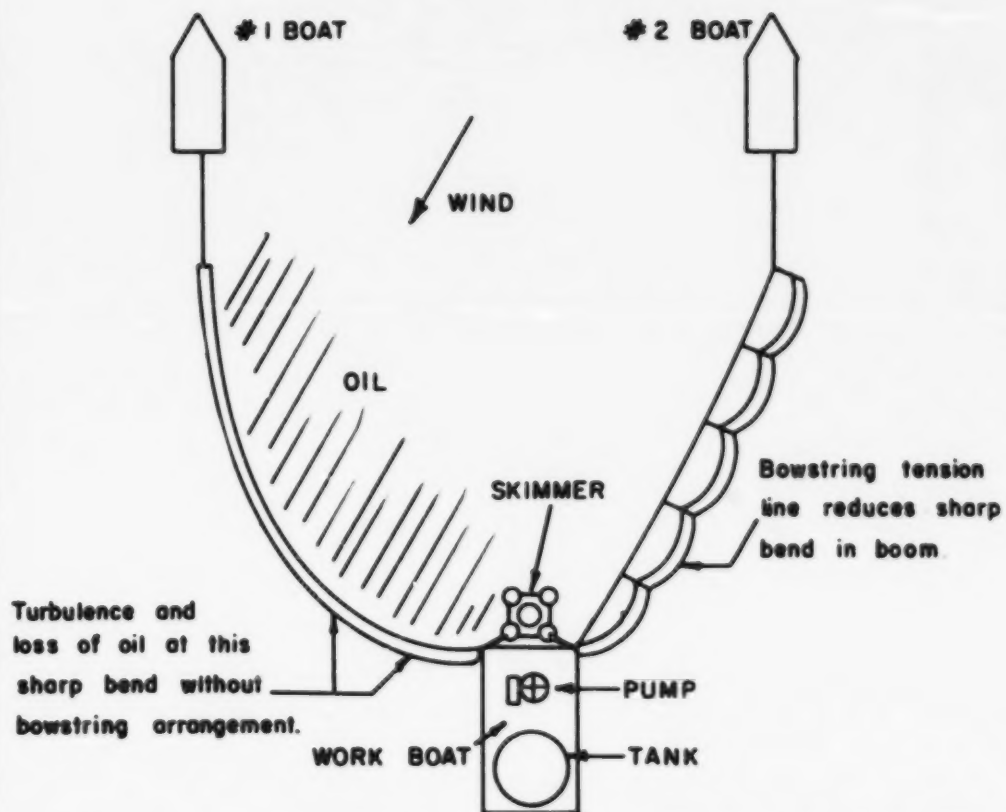
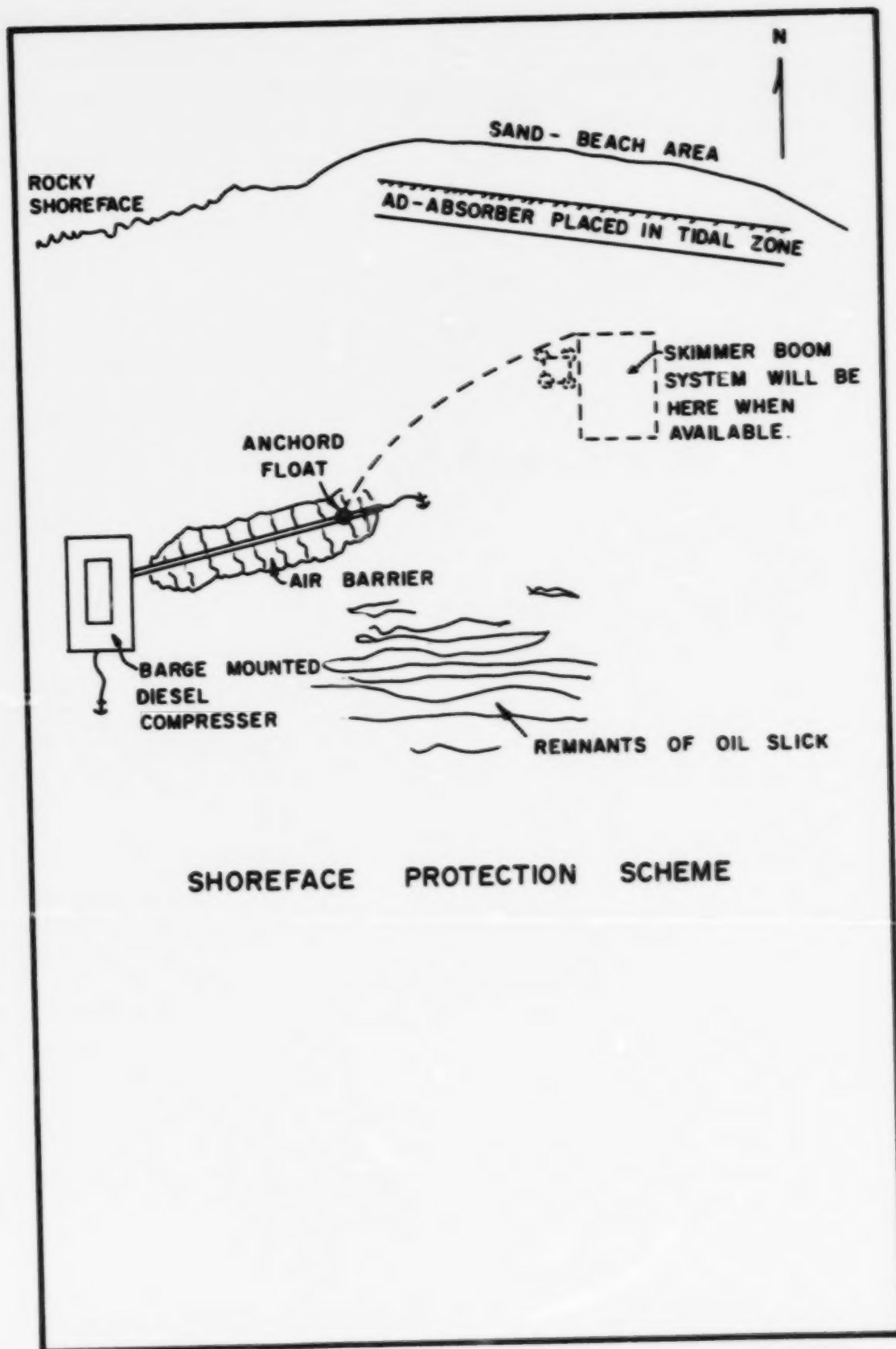


FIGURE C. TOWING A FUNNEL BOOM ARRANGEMENT



SHOREFACE PROTECTION SCHEME

FIGURE 1

the three boats is essential for proper functioning of this system.

It is now necessary to consider setting up some type of protection at the beach area. As all that is left is the air barrier, this will have to be implemented. The air barrier should be placed on the bottom at a distance from shore that will provide it with a minimum of 10 feet of water at low tide. The air supply can come from a diesel powered air compressor mounted on a barge or convenient headland if available. Taking a look at the area, the most difficult area to clean is going to be the rocky section on the northwest side of the beach. The air barrier should be set up so as to divert the oil from the rocky section toward the beach area. A physical absorber should be placed along the tidal zone of the beach area to absorb as much of the oil as possible to prevent penetration into the beach sand. A float with some type of anchoring system has been established a short distance from the end of the air barrier so that the work barge and skimmer, when they arrive at this point, will have somewhere to attach their fence boom. Initially, the oil that has gotten away from the two skimmers working in the bay will be diverted toward the beach. When the main skimming apparatus arrives on scene, the oil will be diverted along the air barrier to the fixed mechanical barrier to the skimmer. (See Figure D)

This is a simplified discussion of boom placement which does not attempt to take into account all of the variables which might be encountered. It is cited as an example of some of the procedures which could be implemented making use of the information presented in Sections I through IV. It must be emphasized, that getting the boom out and corralling the mess is only the beginning. The very difficult task of removing the material from the environment and its ultimate disposal has to be as well considered and

planned out as your boom purchasing and implementation program. There would have been nothing more useless, for example, than taking all of the barrier that you had available in the incident cited above and drawing it across the beach area and then sitting back and watching the oil pile up along its face to finally run under and/or over it to contaminate the beach area. The best designed equipment, if not properly used, will not do the job.

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OIL SKIMMING DEVICES

I INTRODUCTION

A Once an oil spill has occurred, the most positive approach to protect the environment is to physically remove the oil from the water. This may be accomplished, to a more or less degree, by the use of mechanical pickup devices commonly called "skimmers". The numerous types of skimmers presently under development do not permit a presentation on each particular unit. If the reader desires information on particular devices, the Edison Water Quality Laboratory's May 1970 publication titled, "Oil Skimming Devices", is recommended.

B The ideal oil skimmer should be designed for:

- 1 Easy handling.
- 2 Easy operation.
- 3 Low maintenance.
- 4 Ability to withstand rough handling.
- 5 Versatility to operate in various wave and current situations.
- 6 Ability to skim oil at a high oil to water ratio.

The present day skimmers are generally designed to emphasize one or more of the above characteristics. Before purchasing a skimmer

for use in a particular area, the buyer should know what he requires and which characteristics best suit his needs.

The reports and studies which are referenced at the end of this outline evaluate oil skimming devices. Using this information we will now direct our effort towards selecting pieces of equipment which will meet particular needs.

II THE BASIC OIL SKIMMING DEVICES

A Mechanical devices which physically remove oil from the water's surface contain three basic components:

- 1 The pickup head.
- 2 The pump system.
- 3 The oil/water separator.

These components may be constructed as one unit, separate units or any combination of the three. A brief discussion of each follows.

B The pickup head - Figure 1 shows the three most popular types of pickup heads in use today:

- 1 Weir type.
- 2 Floating suction type.
- 3 Adsorbent surface type.

The weir type removes oil from the water's surface by allowing the oil to overflow a weir into a collecting device and holding the water back against the weir. The efficiency of weir pickup heads is highly dependent on calm water conditions and an adequate thickness of oil; however, viscosity of the oil is not too important. Even so, a certain amount of water is drawn over the weir making it necessary to provide a means for separating the oil and water. Therefore, this type of pickup head would be used in areas where the water conditions are generally calm and the oil slick thickness can be maintained at greater than 1/4 inch. The type of oil is not a major consideration.

The floating suction type operates on the same principal as the household vacuum cleaner. The unit is generally small in size and is connected to the oil/water separation section by either a suction or a pressure hose. The floating head may limit the amount of water either by a system of weirs or by the design of the intake openings. Water surface conditions and oil viscosity greatly effect the efficiency of these devices. The floating suction heads are well suited for working in tight areas such as around piers and ships. Debris and sorbents tend to clog these units quite readily and therefore must be considered.

The adsorbent surface type

operate on the principle that a hydrophobic and oleophilic surface will be preferentially wetted by oil and not water. As the adsorbent surface is drawn through the slick oil will cling to it. This oil is then removed either by rollers, wringers or wiper blades. The surfaces are constructed of aluminum or various oleophilic foams or fibers.

The problem of additional oil/water separation is eliminated with these devices. They have been tested successfully in wave heights up to 2 feet. Debris interferes with their efficiency and in some cases may cause severe damage. These units would be best suited for open harbor use. The type of oil to be collected determines the type of adsorbent surface required. For example, heavy oils tend to clog foams and fibers and light oils are not picked up efficiently on aluminum surfaces.

We have pointed out several parameters which will effect the selection of a particular pickup head:

- 1 Type of oil.
- 2 Sea state - waves and currents.
- 3 Debris - sorbents.

4 Physical restrictions — piers, etc.

5 Equipment available to separate oil/water mixtures.

C The Pump System — Pumps and other accessories used with skimmers need to have the following features incorporated in their designs:

- 1 Dependability — carburetors, magnetos, points and plugs need to be protected against ocean air and salt spray.
- 2 Portability — easy to transport. Equipment must have good balance and good handles for manual lifting, and sling attachments for mechanical lifting.
- 3 Quick and positive coupling and uncoupling of hoses and other connections is essential.
- 4 Low maintenance costs and easy cleaning and storage arrangements.
- 5 Ability to work in gangs to handle increased volumes.
- 6 Protection from clogging due to debris or sorbents.

The selection of the type of pump is very important. A centrifugal pump can handle large volumes of flow which may be required to remove very thin slicks. However, this type of pump imparts tremendous mixing energy and produces an oil/water emulsion which may not separate satisfactorily in the

settling chamber. On the other hand, positive displacement pumps, such as diaphragm or piston pumps, while they cannot handle as large a flow, do not mix or emulsify the oil/water mixture. The efficiency of the settling chamber is thus increased. Positive displacement pumps also are very easy to repair, unclog and maintain and do not require priming.

Here, the choice of a pump depends on the volume of water flow required, the size of the oil/water separator available and the expected amount of maintenance assistance available. Based on past experience, the chief cause for an unsuccessful oil skimming operation has been due to failure in the pumping system.

D The Oil/Water Separator — is essentially a settling chamber where collected oil separates by gravity from collected water. A system of weirs and baffles may be employed to facilitate separation. The water may either be pumped out or forced out by gravity. The oil is normally pumped out when the tank has reached its oil storage capacity. The separator may be nothing more than a tank truck or it may be specially designed to meet particular needs.

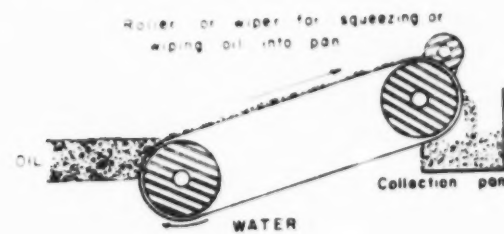
Three types of skimmers



1. Weir type



2. Floating suction type



3. Absorbent surface type

Figure 1

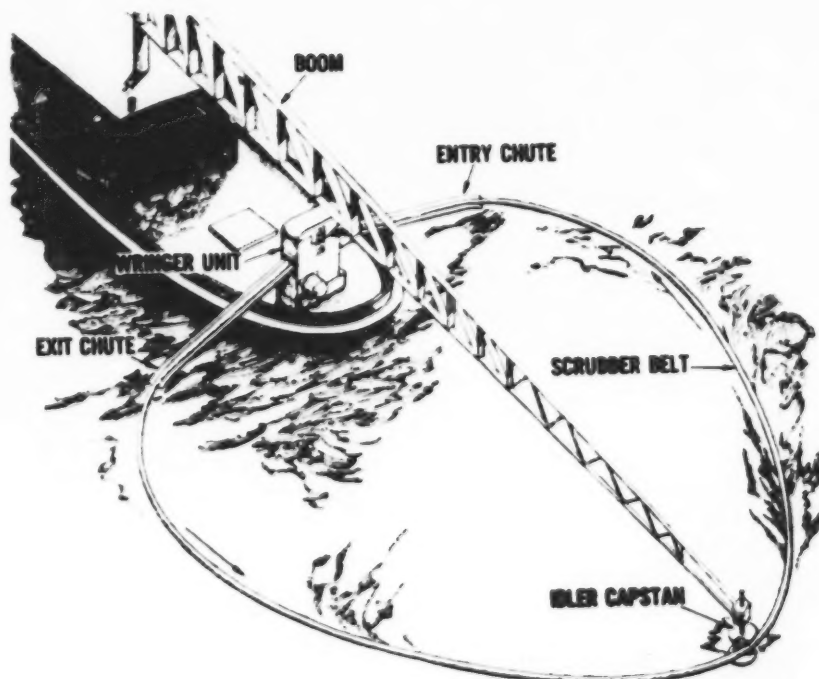


Figure 2 Absorbent Belt for Oil Skimmer

Normally, the weir type and the floating suction head type pick-up units require an oil/water separator. Likewise, if a centrifugal pump is used, a separator is usually required.

III SUMMARY

A The basic oil skimmer is composed of three units:

- 1 Pickup head.
- 2 Pump system.
- 3 Oil/Water Separator

There are three basic pickup heads in use today:

- 1 Weir type.
- 2 Floating suction head type.
- 3 Adsorbent surface type.

The pump system usually employs either of two types of pumps:

- 1 Centrifugal Pump.
- 2 Positive Displacement Pump.

An oil/water separator is required to separate the large amounts of water usually picked up with the oil slick.

B Tests and experiences have indicated that present day skimmers do not operate efficiently in wave heights greater than 1.5 to 2.0 feet or in currents greater than 1.0 to 1.5 feet per second.

C Prior to purchasing an oil skimmer, the buyer should determine physical restrictions, such as piers, shallow water, marshes, etc., estimate the quantities and types of oil to be handled, investigate the local weather conditions and become familiar with the body of water in which the proposed skimmer is to be used. Using this information the proper oil skimmer can then be selected.

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Outline prepared by J. S. Dorrier, Acting Chief, Oil Pollution R&D, Edison Water Quality Laboratory, Edison, New Jersey 08817, January 1971.

BEACH CLEANUP

I INTRODUCTION

National and international publicity given to the Torrey Canyon and Santa Barbara incidents have led to a public outcry to stop the oil pollution of our national shorelines.

II QUESTIONS ON BEACH CLEANUP

The question is often asked, "How do you clean an oil polluted beach?" The answer to this question is relative. What is the composition of the beach? Is it fine grain sand; is it coarse sand; is it pebble or shingle beach? What type of oil pollution has fouled the beach? Was it a #2 oil, #6 or a crude oil? How deep is the oil penetration? What is the temperature and the season? Where is the beach located? Does it have access roads? Can it be reached or traversed by wheeled vehicles or can it only accomodate tracked vehicles? Before we can even begin to answer a question on beach cleanup, we must know as many background facts as possible.

III CLEANUP METHODS

A It has often been said that nature is the best cleaning agent in the world. This is especially true of rocky shores and stone beaches. But if anyone reports that nature removed oil from a sand beach - dig a little deeper - literally. What nature cannot remove, it covers up. Wind blown sand and the seasonal movement of beaches have a tendency to cover man's mistakes.

B The most elementary method of beach cleanup is with the use of rakes, shovels and manpower. If the penetration of oil into the sand is less than two inches

and the oil is not too fluid, the oil can be raked into windrows of approximately one foot and picked up with shovels to be placed into a front loader or dump truck. If the oil is not sufficiently weathered to be viscous, it can be made more workable through the application of a cold water spray from a garden hose or a fire hose.

C If the pollution damage to the beach is much more extensive, then mechanical equipment must be used. Through research, it has been determined that a Motorized Elevating Scraper used in tandem with a motorized scraper, are the best mechanical equipment to be used in beach restoration. The combined uses of these vehicles provide the most rapid means of beach restoration and in addition their use results in the removal of the least amount of excess beach material. Before allowing mechanical equipment on the beach, the operators of these vehicles must be cautioned as to what oil beach sand is to be removed.

IV PREVENTION

A It is much easier to clean up a beach if the oil is stopped at or near the water line. An effective method of protecting a high beach from the onslaught of oil pollution is to throw up a sand berm approximately three feet high. This can be accomplished with the use of earth moving equipment or, if necessary, by hand labor. The artificial berm should be placed along the high water mark, to protect the dry sand above the waterline zone. If the surf is breaking or very shallow, or if there is a current or high tide, the artificial berm should be destroyed. Shovelers can dig down the artificial berm with a garden hose or a fire hose and remove the oil.

B Should sufficient time exist between the notification of an oil spill and its reaching the shore face, one method of alleviating the damage to the beach is the extensive use of straw, either alone, or used in conjunction with the commercial "sorbents". Straw, which has a natural absorptive capacity for oil, will absorb between four and ten times its own weight in oil. To be most effective, the straw should be laid along the low-water mark and as the tide and oil move up the beach, the straw should be worked into the oil, either through natural wave action or mechanical methods.

C If the oil is still washing ashore a series of deep pits can be gouged out of the sand at the water's edge to allow the oil to collect in sufficient thickness to permit removal by vacuum tank trucks.

7. CHEMICALS

We firmly believe that the use of dispersants, emulsifiers and other chemicals is entirely unjustified in the cleanup of oil polluted beaches. In both the Torrey Canyon and Ocean Eagle incidents, it was noted that the use of dispersants on sand caused the sand to become "slick", making it difficult to walk on and leaving a disagreeable odor on the treated sand. However, other reports state that sand "slicked" with oil alone. As the literature on this subject is very vague, further research by the government and private industry seems indicated.

B In oil penetration tests conducted at Sandy Hook, N. J., it was concluded that various types of persistent oil alone penetrated no

more than two inches into the sand while oil mixed with chemicals (dispersants, emulsifiers, etc.) caused penetration of the mixture into the sand at least three times the depth of the untreated oil.

C Application of chemicals to an oil soaked beach and subsequent hosing down of the mixture with sea water, the sand appeared cleansed of oil. However, further investigation revealed that this observation was deceptive, as the oil and chemical mixture was found between four and twelve inches, in irregular bands, below the surface of the sand.

8. BURNING

Many attempts have been made to burn oil on the shore face. Through an extensive literature search and personal observation it is concluded that the burning of oil "in situ" on a contaminated beach is not very practicable. It has been tried with commercial burning agents, flame throwers, "oxygen tiles" and various mixtures of kerosene and gasoline, but all have met with no success. Small, "fresh" pools of heavy crude or light oil can be burned successfully if their lighter ends have not evaporated, but this is a patchy operation at best and is not recommended for cleanup of massive spills.

9. CLEANUP OF LIGHT OILS

Sometimes a "high-use" beach becomes stained with a light oil such as a #2 fuel. This becomes a problem because of instant and deep penetration. The only really effective method of cleansing this type of pollution is to expose as much of the contaminated beach sand to the sunlight and wind as possible. This can be done effectively by the use of a harrowing plow or beach cleaning machines, which are used to remove trash from beaches.

Number two fuel, in contrast to #6 or Bunker "C" fuel oil, contains a relative high amount of light ends. If these light ends are exposed to evaporation through wind and weather, they will dissipate rather rapidly.

- F To accelerate the evaporation and dissipation of #2 fuel from the beaches, a mat of straw should be laid on the beach, at least one inch thick. A disk-harrow should then be used to work the straw down into the sand column so the straw can absorb as much of the oil as possible. A beach cleaning machine should then be used to retrieve the oil soaked straw. The beach should then be harrowed or mechanically raked to hasten the dissipation of the remaining oil trapped in the sub-surface of the sand.

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